

**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			

** 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)

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

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

$$W_{\text{net}} = -500\text{J}$$

$$\text{Therefore Discarded heat} = 1500\text{ J} - 500\text{ J} = 1000\text{J}$$

(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 ($PV = nRT$), prove that C_p is always larger than C_v . You have to show the detailed steps arriving at your final answer.

(Answers)

$$(b) \text{ Isochoric process; } \Delta V = 0$$

$$\text{if gas in a flask is heated } \rightarrow w = -P \Delta V = 0$$

$$\therefore \Delta E = (3/2)nR\Delta T = q + w = q_v \text{ (at constant V)}$$

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

$$\text{heat capacity } C_v = 3/2 nR \text{ at constant volume.}$$

$$\text{Isobaric process } (\Delta P = 0) \rightarrow \text{heat, work are exchangeable}$$

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

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

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

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

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

$$\text{heat capacity } C_p = 5/2 nR \text{ at constant pressure}$$

$$C_p - C_v = nR,$$

$$\therefore C_p > C_v$$

[2] (22 pts)

(a) (10 pts) Choose the substance from each pair with higher absolute entropy S°_{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. $\text{Fe}^{3+}(\text{aq})$, $\text{Fe}^{2+}(\text{aq})$ (Answer) **A. $\text{Fe}^{2+}(\text{aq})$** , _____
- B. $\text{NO}_2^{-}(\text{aq})$, $\text{NO}_3^{-}(\text{aq})$ (Answer) **B. $\text{NO}_3^{-}(\text{aq})$** , _____
- C. $\text{CH}_3\text{OH}(\text{l})$, $\text{CH}_3\text{OH}(\text{g})$ (Answer) **C. $\text{CH}_3\text{OH}(\text{g})$** , _____
- D. $\text{Cl}_2\text{O}(\text{g})$, $\text{Cl}_2(\text{g})$ (Answer) **D. $\text{Cl}_2\text{O}(\text{g})$** , _____
- E. $\text{Na}(\text{l})$, $\text{Na}(\text{s})$ (Answer) **E. $\text{Na}(\text{l})$** _____

(b) (6 pts) For the following chemical reactions, guess the sign of ΔH° . 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. $\text{H}^{+}(\text{aq}) + \text{OH}^{-}(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$ (Answer) **A. $\Delta H^{\circ} < 0$** , _____
- B. $2\text{CO}_2(\text{g}) \rightarrow 2\text{CO}(\text{g}) + \text{O}_2(\text{g})$ (Answer) **B. $\Delta H^{\circ} > 0$** , _____
- C. $\text{HCl}(\text{g}) + \text{NH}_3(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$ (Answer) **C. $\Delta H^{\circ} < 0$** _____

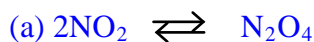
(c) (6 pts) For the following chemical reactions, guess the sign of ΔS° . You will get 2 pt for a correct answer, 0 pt for no answer, and **-1 pt for a wrong answer**. You don't have to explain the reason for your answer.

- A. $\text{H}^{+}(\text{aq}) + \text{OH}^{-}(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$ (Answer) **A. $\Delta S^{\circ} > 0$** , _____
- B. $2\text{CO}_2(\text{g}) \rightarrow 2\text{CO}(\text{g}) + \text{O}_2(\text{g})$ (Answer) **B. $\Delta S^{\circ} > 0$** , _____
- C. $\text{HCl}(\text{g}) + \text{NH}_3(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$ (Answer) **C. $\Delta S^{\circ} < 0$** _____

[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)



$$P_{\text{NO}_2} = P - x \text{ and } P_{\text{N}_2\text{O}_4} = x$$

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

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

$$P_{\text{N}_2\text{O}_4} = 0.686 \text{ atm}, P_{\text{NO}_2} = 0.314 \text{ atm}$$

(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.

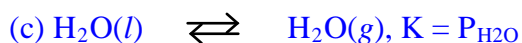
- A. Water vapor in air with 100% relative humidity.
- B. Pure water.
- C. Water in a mixture of 1 ethanol - 1 water (molar ratio)
- D. Water in a mixture of 10 ethanol - 1 water (molar ratio).

(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)



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

$$T = 82.6^\circ\text{C}$$

(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)



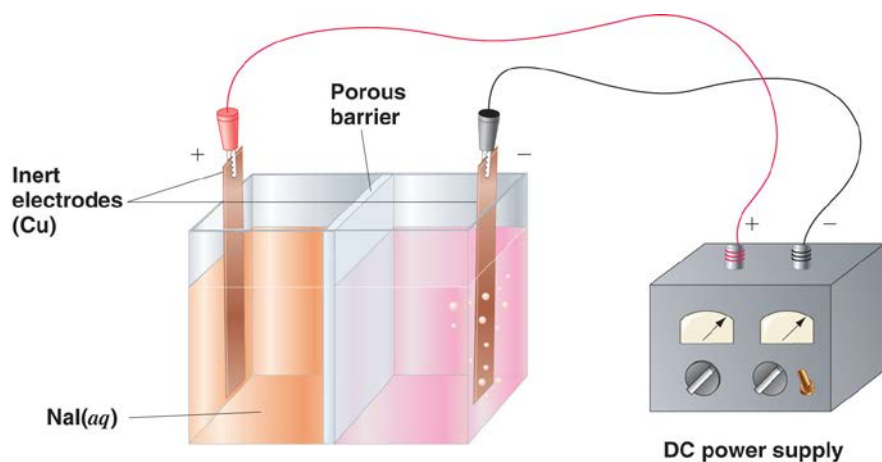
$$K = \frac{K_a K_b}{K_w}$$

(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 $\text{HOOCCH}_2\text{NH}_2$ 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



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



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



(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)

$$(4.0\text{A})(150.\text{s})$$

$$\times(1 \text{ mol e}^-/96500 \text{ C})$$

$$\times(1 \text{ mol I}_2/ 2 \text{ mol e}^-)$$

$$\times(254\text{g I}_2 / 1 \text{ mol I}_2) = 0.79 \text{ g}$$

0.79g of I₂ 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 $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\ell)$ 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 H₂ 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

**2008 FALL Semester Final 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	/27	3	/27	/110
2	/28	4	/28	

** This paper consists of 10 sheets with 4 problems. Please check all page numbers before taking the exam.

Please take a good use of the reference materials (Page 9 and 10), which include (a) Fundamental constants, (b) Conversion factors, and (c) Atomic weights of the elements. 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 (30% deduction).

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

1. Period, Procedure, and Location

1) Distribution and Correction Period: **December 20 (SAT), 10:00 a.m. ~ 13:00 p.m.**

2) Procedure: During the period, you can take your final examination 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 paper with a stapler (Please, write your name, professor, and class.). Put them into a paper box in front of elevator. The papers with the claims will be re-examined by TA.

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

3) Location: Lobby (1st floor), Goong-Ni Laboratory Building

2. Final Confirmation

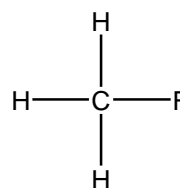
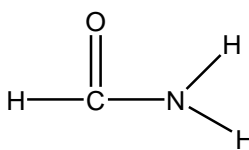
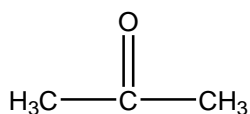
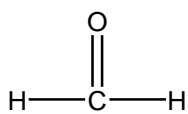
1) Period: **December 23(TUE)**

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.

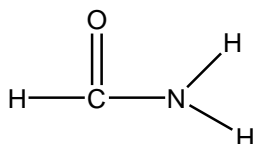
[1] (27 pts)

(a) (4 pts) Which substance has hydrogen bonding as intermolecular forces?



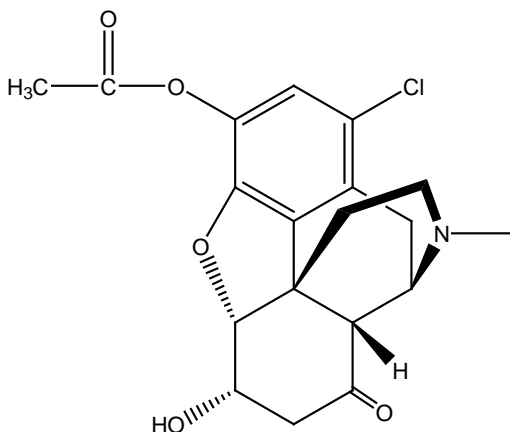
(Answers)

(a)

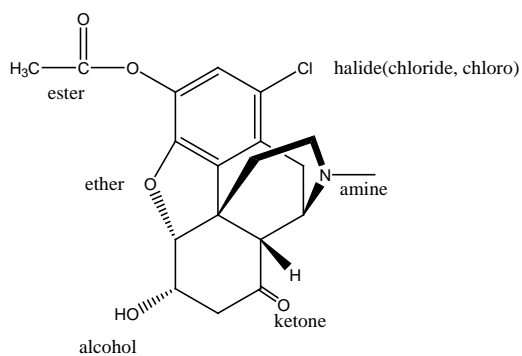


(b) (6 pts) The following organic molecule is morphine, a powerful pain reliever, yet very addictive. It has a pentacyclic structure with several functional groups. Indicate all functional groups and write the name besides each functional group. (1 pt for each correct answer)

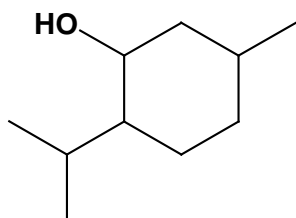
(Answers)



(b)

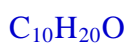


(c) (17 pts) The molecule shown in skeletal representation below is menthol, a crystalline organic compound having local anesthetic and counterirritant properties. What is the formula of menthol (3 pts)? How many chiral centers (asymmetric carbons) does it have (3 pts)? Indicate them on the structure (3 pts). How many stereoisomers are possible (do not count conformational or geometrical isomers) (3 pts)? Draw most stable stereoisomer in a chair form (5 pts).

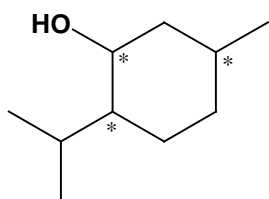


(Answers)

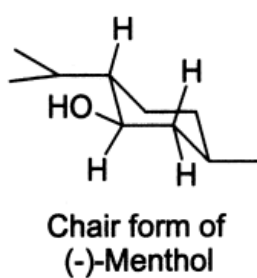
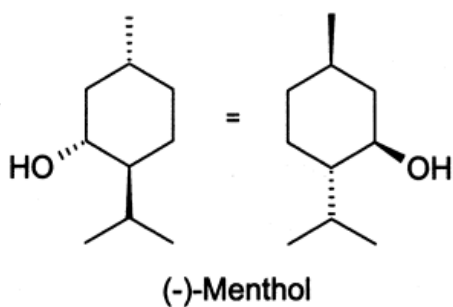
(c)



3 chiral centers. 8 isomers.



Most stable isomer is:



[2] (28 pts)

(a) (2 pts) Which element among the 3d transition metals can have the oxidation state of 1+.

(Answers)

Cu

(b) (4 pts) Among compounds of the early transition elements, KMnO_4 shows a very intense color in solution. What is the reason?

(Answers)

It is because of the charge-transfer electronic transition from an oxygen-like orbital to a metal-like orbital.

(c) (22 pts) The octahedral complex $[\text{CoCl}_2(\text{en})_2]\text{Cl}$ is a low spin complex.

1) (4 pts) Name this compound.

(Answers) Dichlorobis(ethylenediamine) Cobalt (III) chloride

2) (4 pts) What is the oxidation state of the cobalt?

(Answers) oxidation state = +3

3) (4 pts) If the crystal field energy splitting is 1 kcal/mol, what is the crystal field stabilization energy (CFSE) of this complex?

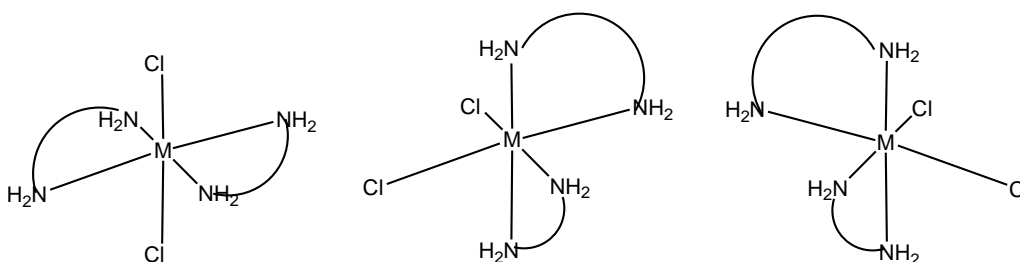
(Answers) $\text{CFSE} = -12/5 \text{ kcal/mol}$

4) (4 pts) Is the complex paramagnetic or diamagnetic?

(Answers) Diamagnetic

5) (6 pts) Draw all possible isomers of the complex.

(Answers) three isomers



[3] (27 pts)

(a) (3 pts) We have learned the *half-life* or *half-reaction time* $t_{1/2}$. Its definition is the time needed for half of the reactant molecules to disappear. Now, instead of half-reaction time, let us define a new term called *lifetime* τ . The definition of *lifetime* is the time at which the reactant concentration falls to $1/e$ of its initial value. Express the concentration of the reactant as a function of initial concentration (c_0) and lifetime (τ) for a first-order reaction.

(Answers)

(a) $\tau = 1/k$. Therefore $c(t) = c_0 \exp(-kt) = c_0 \exp(-t/\tau)$

(b) (5 pts) Assuming that the boat \rightarrow chair conversion in cyclohexane vapor has a preexponential factor of $1.0 \times 10^{13} \text{ s}^{-1}$ and an activation energy of 10.1 kcal/mol, estimate the *lifetime* for unimolecular conversion at 25 °C. (2 pts for the correct concept and 3 pts for the correct final answer)

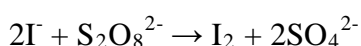
(Answers)

(b)

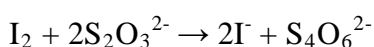
$$k = \frac{1.0 \times 10^{13}}{\text{s}} \exp\left(\frac{-10.1 \text{ kcal/mol}}{0.0019872 \text{ kcal/K mol}(298.15 \text{ K})}\right) = 3.95 \times 10^5 / \text{s}.$$

$$\tau = 1/k = 2.53 \times 10^{-6} \text{ s}.$$

(c) (19 pts) An interesting and important method in solution kinetics employs so-called clock reactions, in which a fast but noninterfering reaction is used to scavenge a product of a slower reaction to be studied. One of the earliest known applications of this method was in the study of the oxidation of iodide (I^-) by peroxydisulfate ion ($\text{S}_2\text{O}_8^{2-}$)



A comparatively slow reaction, whose rate is clocked by the fast reduction of I_2 by thiosulfate ion ($\text{S}_2\text{O}_3^{2-}$)



Using a small amount of thiosulfate, and starch indicator to detect the presence of I_2 by formation of a blue complex, the solution will remain clear until the thiosulfate has completely reacted, then “flash” blue as the excess I_2 complexes with starch. (Without the clocking reaction, the blue color

would gradually deepen as the slow oxidation progressed.) Clock reactions are most useful for measuring initial rates. A student obtained the following initial rate data for this reaction:

Run	$[I^-]_0$ (M)	$[S_2O_8^{2-}]_0$ (M)	$[S_2O_3^{2-}]_0$ (M)	t to blue flash (s)
I	0.080	0.040	0.0010	38
II	0.060	0.040	0.0010	52
III	0.080	0.025	0.0010	61
IV	0.020	0.0010	0.0005	???

Use these data to find the rate law (6 pts) and calculate the rate constant for the reaction (6 pts).

Make a numerical prediction of the flash time for run IV (7 pts).

(Answers)

The time data are for the appearance of the blue color, the point at which all of the thiosulfate ions are gone. The rate data are based on the reaction $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$, for which

$$S_2O_3^{2-} \text{ reaction rate} = -\frac{1}{2} \frac{d[S_2O_3^{2-}]}{dt}$$

This is a *fast* reaction that merely times the slow $S_2O_8^{2-}$ reaction, and correspondingly, the thiosulfate ion will not appear in the slow $S_2O_8^{2-}$ reaction rate equation. For run I $d[S_2O_3^{2-}]/dt = 0.0010 \text{ M}/38 \text{ s} = 2.63 \times 10^{-5} \text{ M/s}$. Likewise, runs II and III give $d[S_2O_3^{2-}]/dt = 1.92 \times 10^{-5} \text{ M/s}$ and $1.64 \times 10^{-5} \text{ M/s}$, respectively. Now, the key step is to make the approximation that the thiosulfate reaction is occurring very nearly simultaneously with the

peroxydisulfate reaction, since $S_2O_3^{2-}$ scavenges I_2 as quickly as it is formed. Assuming this, the time data that we have apply to *both* reactions, meaning that the rate of the thiosulfate reaction, obtained from the given time data, will be equal to the rate of the peroxydisulfate reaction. From the above $S_2O_3^{2-}$ reaction rate equation the $S_2O_3^{2-}$ reaction rates are $1.32 \times 10^{-5} \text{ M/s}$, $9.60 \times 10^{-6} \text{ M/s}$, and $8.20 \times 10^{-6} \text{ M/s}$ for the three runs.

Now, assuming that the rate law for the slow reaction is of the form $S_2O_8^{2-}$ reaction rate = $k[I^-]^p[S_2O_8^{2-}]^q$, the method of initial rates can be used. For p

$$\frac{\text{rate I}}{\text{rate II}} = \frac{[I^-]_I^p}{[I^-]_{II}^p} \Rightarrow \frac{1.32 \times 10^{-5} \text{ M/s}}{9.60 \times 10^{-6} \text{ M/s}} = \left(\frac{0.080 \text{ M}}{0.060 \text{ M}} \right)^p$$

Since $\ln x^p = p \ln x$, $p = 1.10 \approx 1$. Likewise for runs I and III, $q = 1.01 \approx 1$. Thus, $S_2O_8^{2-}$ reaction rate = $k[I^-][S_2O_8^{2-}]$. To obtain the rate constant, we substitute in the values for a run and solve the rate expression for k . For run I this gives $k = (1.32 \times 10^{-5} \text{ M/s})/[0.08][0.04] = 4.13 \times 10^{-3} \text{ L/mol s}$. Runs II and III give $k = 4.00 \times 10^{-3} \text{ L/mol s}$ and $4.10 \times 10^{-3} \text{ L/mol s}$, respectively. The average of these three is $k = 4.08 \times 10^{-3} \text{ L/mol s}$.

To determine the time for run IV, we calculate its initial rate. The rate of the thiosulfate reaction is given by

$$S_2O_3^{2-} \text{ reaction rate} = \frac{4.08 \times 10^{-3} \text{ L}}{\text{mol s}} \left(\frac{0.020 \text{ mol}}{\text{L}} \right) \left(\frac{0.010 \text{ mol}}{\text{L}} \right) = \frac{8.2 \times 10^{-7} \text{ mol}}{\text{L s}}$$

Now, from the above $S_2O_3^{2-}$ reaction rate, the rate at which the thiosulfate ion disappears will be twice this rate, giving $-d[S_2O_3^{2-}]/dt = 1.64 \times 10^{-6} \text{ mol/L s}$. Finally, since $[S_2O_3^{2-}]_0 = 0.0005 \text{ M}$, the time until the blue color flashes is $0.0005 \text{ M}/(1.64 \times 10^{-6} \text{ mol/L s}) = 305 \text{ seconds}$.

Rate law (6pts): rate = $k[I^-][S_2O_8^{2-}]$

Rate constant (6pts): $k = 4.08 \times 10^{-3} \text{ L/mol-s}$

Flash time (7 pts): 3050 s

[4] (28 pts) Consider the following selected values of thermodynamic properties at 298.15 K and 1 atm. Please answer to the following questions by using the information in the given table.

Species	ΔH_f°	ΔG_f°	S°	\bar{C}_p
	(kcal/mol)	(kcal/mol)	(cal/(K · mol))	(cal/(K · mol))
B(s)	0.0	0.0	1.40	2.65
B(g)	134.5	124.0	36.65	4.971
BCl ₃ (l)	-102.1	-92.6	49.3	25.5
BCl ₃ (g)	-96.50	-92.91	69.31	14.99
BBr ₃ (l)	-57.3	-57.0	54.9	30.6
BBr ₃ (g)	-49.15	-55.56	77.47	16.20

(a) (2 pts) For boron, what kind of turnaround temperature can be calculated from the table?

(Answers)

(a) Since the information for B(s) and B(g) are given, the sublimation temperature can be calculated.

(b) (7 pts) The potential energies between molecules in liquids and solids have an inverse-power dependence on the intermolecular distance R, that is $V(R) \propto 1/R^s$. What types of intermolecular interactions are present for BCl₃ and BBr₃ (2 pts)? Indicate the s value for each interaction (2 pts). Among these intermolecular forces, which are always attractive (1 pt)? Which molecules would have higher boiling temperature and why (2 pts)?

(Answers)

(b) instantaneous dipole-induced dipole interaction (Dispersion or London-Dispersion) (s = 6) and dipole-dipole interaction (s = 3). London-Dispersion force is always attractive. BBr₃ would have higher boiling point due to higher LD force. The higher LD force is due to higher polarizability of Br compared with Cl due to higher number of electrons.

(c) (6 pts) Calculate the boiling temperatures of BCl_3 and BBr_3 (3 pts for each, 1 pt for the correct concept and 2 pts for the correct final answer). Show your answer in $^\circ\text{C}$.

(Answers)

$$(c) T_b = \Delta H_{\text{vap}} / \Delta S.$$

For BCl_3 ,

$$T_b = \frac{(-96.50 - (-102.1)) \text{ kcal/mol}}{(69.31 - 49.3) \text{ cal/(K} \cdot \text{mol)}} \\ = 279.86 \text{ K} = 6.7^\circ \text{C}$$

For BBr_3 ,

$$T_b = \frac{(-49.15 - (-57.3)) \text{ kcal/mol}}{(77.47 - 54.9) \text{ cal/(K} \cdot \text{mol)}} \\ = 361.1 \text{ K} = 87.9^\circ \text{C}$$

(d) (7 pts) Calculate the amount of heat needed to raise the temperature of 1 mol BCl_3 from 0°C to 50°C . Show your answer in cal. (4 pts for the correct concept and 3 pts for the correct final answer)

(Answers)

(d) In three steps: 1) from 0°C to 6.7°C , 2) boiling at 6.7°C , and 3) 6.7°C to 50°C .

$$\text{Total heat} = n\bar{C}_p(l)(T_b - T_1) + n\Delta H_{\text{vap}}^\circ + n\bar{C}_p(g)(T_2 - T_b) \\ = (1.00 \text{ mol})(25.5 \text{ cal/K mol})(6.7 - 0)\text{K} + (1.00 \text{ mol})(5600 \text{ cal/mol}) + (1.00 \text{ mol})(14.99 \text{ cal/K mol})(50 - 6.7)\text{K} = 6420 \text{ cal}$$

(e) (6 pts) Estimate the equilibrium vapor pressure of BBr_3 at 25°C . Show your answer in Torr. (3 pts for the correct concept and 3 pts for the correct final answer)

(Answers)

(e) From the table, $\Delta G_{\text{vap},298}^\circ = (-55.56 - (-57.0)) \text{ kcal/mol} = 1.44 \text{ kcal/mol}$.

At equilibrium, $\Delta G_{\text{vap}} = \Delta G_{\text{vap}}^\circ + RT \ln P_{\text{vap}} = G(g) - G(l) = 0$.

$$P_{\text{eq}} = \exp(-\Delta G_{\text{vap}}^\circ / RT) = \exp(-1440 / (1.987 \times 298.15)) = 0.088 \text{ atm} = 67 \text{ Torr}.$$

Fundamental constants

Constant	Symbol	Value (SI units)	cgs-esu or other units
Gas constant	R	$8.31447 \text{ J K}^{-1} \text{ mol}^{-1}$	$8.31447 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$
		$8.31447 \text{ m}^3 \text{ Pa K}^{-1} \text{ mol}^{-1}$	$0.0820575 \text{ L atm K}^{-1} \text{ mol}^{-1}$
Avogadro's number	N_A	$6.02214 \times 10^{23} \text{ mol}^{-1}$	$6.02214 \times 10^{23} \text{ mol}^{-1}$
			$6.02214 \times 10^{23} \text{ amu g}^{-1}$
Faraday constant	F	$96485.3 \text{ C mol}^{-1}$	$23.06055 \text{ kcal V}^{-1} \text{ mol}^{-1}$
		$96.4853 \text{ kJ V}^{-1} \text{ mol}^{-1}$	
Speed of light	c	$2.99792458 \times 10^8 \text{ m s}^{-1}$	$2.99792458 \times 10^{10} \text{ cm s}^{-1}$
Planck's constant	h	$6.62607 \times 10^{-34} \text{ J s}$	$6.62607 \times 10^{-27} \text{ erg s}$
Boltzmann's constant	k_B	$1.38065 \times 10^{-23} \text{ J K}^{-1}$	$1.38065 \times 10^{-16} \text{ erg K}^{-1}$
Electronic charge	e	$1.602176 \times 10^{-19} \text{ C}$	$4.803204 \times 10^{-10} \text{ esu (statC)}$
Coulomb's law constant	k	$8.98755 \times 10^9 \text{ J m C}^{-2}$	$1 \text{ erg cm esu}^{-2}$
Electron mass	m_e	$9.10938 \times 10^{-31} \text{ kg}$	$9.10938 \times 10^{-28} \text{ g}$
			0.0005485799 amu

Conversion factors

Energy into joules (J)

$$4.184 \text{ J/cal} \quad 1.602 \times 10^{-19} \text{ J/eV} \quad 101.325 \text{ J/(L atm)} \quad 10^{-7} \text{ J/erg} \quad 1.986 \times 10^{-23} \text{ J/cm}^{-1}$$

Length into meters (m)

$$10^{-10} \text{ m/\AA} \quad 0.0254 \text{ m/in.} \quad 0.3048 \text{ m/ft} \quad 1609.3 \text{ m/mi}$$

Volume into cubic meters (m³)

$$10^{-3} \text{ m}^3/\text{L} \quad 3.7854 \times 10^{-3} \text{ m}^3/\text{gal}$$

Pressure into Pascals (Pa)

$$101.325 \text{ Pa/atm} \quad 10^5 \text{ Pa/bar} \quad 133.3 \text{ Pa/torr} \quad 6895 \text{ Pa/(lb in.}^{-2}\text{)}$$

Mass into kilograms (kg)

$$0.4536 \text{ kg/lb} \quad 1.66054 \times 10^{-27} \text{ kg/amu}$$

Atomic weights of the elements 2001
<http://www.chem.qmul.ac.uk/iupac/AtWt/>

Z	Symbol	Name	Atomic Wt	Z	Symbol	Name	Atomic Wt
1	H	Hydrogen	1.00794(7)	44	Ru	Ruthenium	101.07(2)
2	He	Helium	4.002602(2)	45	Rh	Rhodium	102.90550(2)
3	Li	Lithium	[6.941(2)]	46	Pd	Palladium	106.42(1)
4	Be	Beryllium	9.012182(3)	47	Ag	Silver	107.8682(2)
5	B	Boron	10.811(7)	48	Cd	Cadmium	112.411(8)
6	C	Carbon	12.0107(8)	49	In	Indium	114.818(3)
7	N	Nitrogen	14.0067(2)	50	Sn	Tin	118.710(7)
8	O	Oxygen	15.9994(3)	51	Sb	Antimony	121.760(1)
9	F	Fluorine	18.9984032(5)	52	Te	Tellurium	127.60(3)
10	Ne	Neon	20.1797(6)	53	I	Iodine	126.90447(3)
11	Na	Sodium	22.989770(2)	54	Xe	Xenon	131.293(6)
12	Mg	Magnesium	24.3050(6)	55	Cs	Cesium	132.90545(2)
13	Al	Aluminum	26.981538(2)	56	Ba	Barium	137.327(7)
14	Si	Silicon	28.0855(3)	57	La	Lanthanum	138.9055(2)
15	P	Phosphorus	30.973761(2)	58	Ce	Cerium	140.116(1)
16	S	Sulfur	32.065(5)	59	Pr	Praseodymium	140.90765(2)
17	Cl	Chlorine	35.453(2)	60	Nd	Neodymium	144.24(3)
18	Ar	Argon	39.948(1)	61	Pm	Promethium	[145]
19	K	Potassium	39.0983(1)	62	Sm	Samarium	150.36(3)
20	Ca	Calcium	40.078(4)	63	Eu	Europium	151.964(1)
21	Sc	Scandium	44.955910(8)	64	Gd	Gadolinium	157.25(3)
22	Ti	Titanium	47.867(1)	65	Tb	Terbium	158.92534(2)
23	V	Vanadium	50.9415(1)	66	Dy	Dysprosium	162.500(1)
24	Cr	Chromium	51.9961(6)	67	Ho	Holmium	164.93032(2)
25	Mn	Manganese	54.938049(9)	68	Er	Erbium	167.259(3)
26	Fe	Iron	55.845(2)	69	Tm	Thulium	168.93421(2)
27	Co	Cobalt	58.933200(9)	70	Yb	Ytterbium	173.04(3)
28	Ni	Nickel	58.6934(2)	71	Lu	Lutetium	174.967(1)
29	Cu	Copper	63.546(3)	72	Hf	Hafnium	178.49(2)
30	Zn	Zinc	65.409(4)	73	Ta	Tantalum	180.9479(1)
31	Ga	Gallium	69.723(1)	74	W	Tungsten	183.84(1)
32	Ge	Germanium	72.64(1)	75	Re	Rhenium	186.207(1)
33	As	Arsenic	74.92160(2)	76	Os	Osmium	190.23(3)
34	Se	Selenium	78.96(3)	77	Ir	Iridium	192.217(3)
35	Br	Bromine	79.904(1)	78	Pt	Platinum	195.078(2)
36	Kr	Krypton	83.798(2)	79	Au	Gold	196.96655(2)
37	Rb	Rubidium	85.4678(3)	80	Hg	Mercury	200.59(2)
38	Sr	Strontium	87.62(1)	81	Tl	Thallium	204.3833(2)
39	Y	Yttrium	88.90585(2)	82	Pb	Lead	207.2(1)
40	Zr	Zirconium	91.224(2)	83	Bi	Bismuth	208.98038(2)
41	Nb	Niobium	92.90638(2)	90	Th	Thorium	232.0381(1)
42	Mo	Molybdenum	95.94(2)	91	Pa	Protactinium	231.03588(2)
43	Tc	Technetium	[98]	92	U	Uranium	238.02891(3)

Source: IUPAC Commission on Atomic Weights and Isotopic Abundances. Values from the 2001 table, *Pure Appl. Chem.* **75**, 1107 (2003). Numbers in parenthesis are uncertainties in least significant digit. For Li, terrestrial sample variations prevent a more precise value. For Tc and Pm, no stable isotopes exist.