

## Chemistry 122; Midterm 3

There are 13 questions worth a total of 75 points on this exam.

Additionally, there is a bonus questions worth 5 points.

This exam consists of 6 double-sided pages.

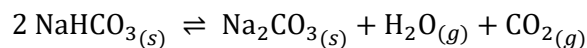
Your name: \_\_\_\_\_Key\_\_\_\_\_

### Multiple-Choice Questions:

Each multiple-choice question is worth 5 points unless otherwise indicated.

Choose the best answer for each.

1. Baking soda undergoes thermal decomposition as follows:



which of the following is (are) acceptable equilibrium constant expressions for the process?

i.  $K_c = \frac{[\text{H}_2\text{O}][\text{CO}_2][\text{Na}_2\text{CO}_3]}{[\text{NaHCO}_3]^2}$

ii.  $K_P = P_{\text{H}_2\text{O}} P_{\text{CO}_2}$

iii.  $K_c = [\text{H}_2\text{O}][\text{CO}_2]$

iv.  $K_c = \frac{[\text{H}_2\text{O}][\text{CO}_2][\text{Na}_2\text{CO}_3]}{[\text{NaHCO}_3]}$

A. i only

B. ii only

C. iii only

D. ii and iii

E. iv only

F. i, ii, and iii

Intended to be easy.

Concentration terms for solids do not occur in equilibrium constant expressions, because they are constant. Terms for the gasses can be expressed either as pressures (ii) or as concentrations (iii). The correct answer is D, ii and iii.

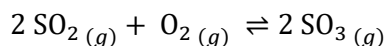
2. Suppose one carries out the thermal decomposition of baking soda (see the reaction above) (a) first in a sealed container. Then, (b) starting with the same amount of baking soda as was used in (a), one carries out the thermal decomposition again in an open container. For which reaction is more carbon dioxide produced?

- A. The one in the sealed container.
- B. The one in the open container.
- C. Neither; the reaction proceeds to the same extent in both cases.

Intended to be easy.

In (a), the carbon dioxide and water that are evolved build up in the sealed chamber until their equilibrium pressures are established, at which point the reaction proceeds no further – it is at equilibrium. In (b) however, carbon dioxide and water pressures do not build up at all – the gasses simply disperse into the atmosphere – and never reach their equilibrium pressures. So the reaction continues until all the baking soda has decomposed. The correct answer is B. Note that this is an application of Le Châtelier's Principle: the product is continually being removed by dispersal in the atmosphere, so the reaction continues to proceed to the right until the reactant is exhausted.

3. The equilibrium constant for the reaction:



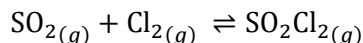
is  $5.60 \times 10^4$  at 350 °C. If initial pressures of  $\text{SO}_2$  and  $\text{O}_2$  in a mixture are 0.350 atm and 0.762 atm respectively, at equilibrium, will the total pressure be less than, greater than, or the same as, the sum of these initial pressures?

- A. Greater than.
- B. Less than.
- C. The same as.

Intended to be easy.

The problem gives no initial pressure for the product, nor any means of computing it, so we must infer that its initial pressure is 0. Note that the reaction combines three moles of reactants to form two moles of products. If this reaction proceeds to any extent at all the overall pressure must. One can be confident that the reaction will proceed because of the large equilibrium constant. The correct answer is B.

3. Consider the following equilibrium system:



for which  $\Delta H = -67 \text{ kJ / mol}$ . Suppose that once this system has reached equilibrium, additional  $\text{SO}_2\text{Cl}_2$  is added. What will be the effect(s)?

- i. The concentrations of  $\text{SO}_2$  and  $\text{Cl}_2$  will increase.
- ii. The temperature will increase.
- iii. The temperature will decrease.

- A. i only
- B. ii only
- C. i and ii
- D. i and iii

Intended to be medium because you have to draw two conclusions instead of one.

Recall that in Le Châtelier's Principle problems, heat is to be considered a product if the reaction is exothermic, and a reactant if the reaction is endothermic. Here,  $\Delta H < 0$ , so the reaction is exothermic. The addition of  $\text{SO}_2\text{Cl}_2$  will cause the reaction to proceed to the left – backwards – in the endothermic direction. Therefore, the concentrations of  $\text{SO}_2$  and  $\text{Cl}_2$  will increase, and the heat will decrease. The correct answer is D.

4. The decomposition of ammonium hydrogen sulfide has the following chemical equation:



Suppose 0.121 mol of ammonium hydrogen sulfide are placed in an evacuated 4.00 L vessel and the system is allowed to come to equilibrium. At this point it is observed that some solid remains, and that the pressure is 0.709 atm. What is  $K_p$  for the reaction?

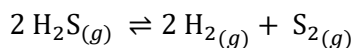
- A. 0.355
- B. 0.709
- C. 0.126
- D. 0.503

Intended to be medium: requires the algebraic computation, and application, of  $P_T$ .

The detail that solid remains indicates that equilibrium has been reached. So, we know that the total pressure of ammonia and hydrogen sulfide gasses together is 0.709 atm. We know further from the stoichiometry of the reaction that those two gasses must

each have the same partial pressure, which allows us to determine that each pressure is  $0.709 \text{ atm} / 2 = 0.355 \text{ atm}$ . The equilibrium constant is then  $(0.355)^2 = 0.126$ ; C is the correct answer.

5. At  $1130^\circ\text{C}$  the equilibrium constant ( $K_c$ ) for the reaction:



is  $2.25 \times 10^{-4}$ . If at equilibrium  $[\text{H}_2\text{S}] = 4.84 \times 10^{-3} \text{ M}$  and  $[\text{H}_2] = 1.50 \times 10^{-3} \text{ M}$ , calculate  $[\text{S}_2]$ .

- A.  $4.84 \times 10^{-2} \text{ M}$
- B.  $7.26 \times 10^{-4} \text{ M}$
- C.  $2.34 \times 10^{-3} \text{ M}$
- D.  $4.63 \times 10^4 \text{ M}$

Intended to be medium, primarily due to the algebra required. But the problem is just plugging and chugging into the equilibrium constant expression:

$$K_{eq} = \frac{[\text{H}_2]^2 [\text{S}_2]}{[\text{H}_2\text{S}]^2} = 2.25 \times 10^{-4}$$

$$\frac{(1.50 \times 10^{-3})^2 [\text{S}_2]}{(4.84 \times 10^{-3})^2} = 2.25 \times 10^{-4}$$

$$[\text{S}_2] = \frac{(2.25 \times 10^{-4}) (4.84 \times 10^{-3})^2}{(1.50 \times 10^{-3})^2}$$

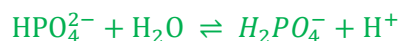
$$[\text{S}_2] = 2.34 \times 10^{-3}$$

The correct answer is C.

6. What is the conjugate acid of  $\text{HPO}_4^{2-}$ ?

- A.  $\text{H}_2\text{PO}_4^-$
- B.  $\text{PO}_4^{3-}$
- C.  $\text{H}_3\text{PO}_4$
- D.  $\text{HPO}_4^{2-}$  is a conjugate base; it doesn't have a conjugate acid.

Intended to be medium: you had to think backwards from a base to get a conjugate acid.



In the reaction above,  $\text{HPO}_4^{2-}$  behaves as a base to abstract a proton from water and produce its conjugate acid,  $\text{H}_2\text{PO}_4^-$ . The correct answer is A.

7. What is the pH of a solution that is  $2.8 \times 10^{-4}$  M in  $\text{Ba}(\text{OH})_2$ ?

- A. 3.25
- B. 11.45
- C. 10.75
- D. It is impossible to decide unless we are also given  $K_B$ .

If  $[\text{Ba}(\text{OH})_2] = 2.8 \times 10^{-4}$  M, then  $[\text{OH}^-] = 2 (2.8 \times 10^{-4} \text{ M}) = 5.6 \times 10^{-4}$  M.

$$\text{pOH} = -\log (5.6 \times 10^{-4}) = 3.25.$$

$$\text{pH} = 14 - 3.25 = 10.75.$$

The correct answer is C.

8. The  $K_a$  for benzoic acid is  $6.5 \times 10^{-5}$ . What is the pH of a 0.10 M solution of benzoic acid?

- A. 2.01
- B. 1.01
- C. 2.72
- D. 2.60

Intended to be medium principally because of the algebra required.

An ICE table:

	[Benzoic acid] (M)	[H <sup>+</sup> ] (M)	[Benzoate] (M)
Initial	0.1	0	0
Change	-x	+x	+x
Equilibrium	0.1 - x	x	x

provides the quadratic:

$$\frac{x^2}{0.10 - x} = 6.5 \times 10^{-5}$$

Rearranging into standard form:

$$x^2 = 6.5 \times 10^{-5} (0.10 - x)$$

$$x^2 + (6.5 \times 10^{-5})x - 6.5 \times 10^{-6} = 0$$

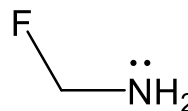
which is solved by the quadratic formula to afford  $x = 2.52 \times 10^{-3}$ . The negative logarithm of this quantity is 2.60; D is the correct answer.

9. Consider the following acids: FCOOH, ClCOOH, BrCOOH, and HCOOH, which are listed in order of decreasing strength. That is fluoroformic acid is stronger than chloroformic acid, which is stronger than bromoformic acid, which is stronger than formic acid. Clearly, the more electronegative the group attached to a (carboxylic) acid is, the stronger the acid is. The situation is opposite for bases: the *more electron density* attached to a basic group, the *stronger the base* is. Using this information, order the following bases from strongest to weakest. Note that a carbon chain *contributes* electron density to a basic group.

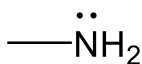
i:



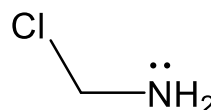
ii:



iii:



iv:



- A.  $\text{i} > \text{ii} > \text{iv} > \text{iii}$
- B.  $\text{ii} > \text{iv} > \text{iii} > \text{i}$
- C.  $\text{iii} > \text{iv} > \text{ii} > \text{i}$
- D.  $\text{i} > \text{iii} > \text{iv} > \text{ii}$

Intended to be difficult: You are required to assimilate a variety of pieces of information and apply them to a circumstance to which you have not previously been introduced.

One can immediately identify (i) as the weakest base, because it has no alkyl group attached to it. If one also recognizes that (ii) and (iii) have electron withdrawing groups on them, it becomes clear that (iii) must be the strongest base. Fluorine withdraws electrons more strongly than Cl, making (ii) weaker than (iv). Therefore, the proper order is option C:





10. Match each of the following oxides in the left hand column with an appropriate characterization in the right hand column. You may need to use items in the right hand column more than once.

Intended to be easy.

CaO

Match: \_\_\_\_ii\_\_\_\_

i: acidic oxide

Al<sub>2</sub>O<sub>3</sub>

Match: \_\_\_\_iii\_\_\_\_

ii: basic oxide

SO<sub>3</sub>

Match: \_\_\_\_i\_\_\_\_

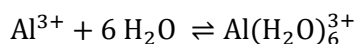
iii: amphoteric oxide

ClO<sub>3</sub>

Match: \_\_\_\_i\_\_\_\_

### Problems:

11. (5 points) If AlCl<sub>3</sub> is dissolved in aqueous solution, complete dissociation of the ions occurs. However, Al<sup>3+</sup>, being very highly charged, undergoes a further reaction with water:

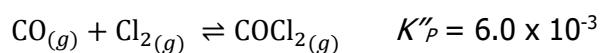
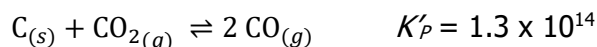


This reaction can be interpreted as a Lewis acid / base reaction. Identify the Lewis acid(s) and base(s), and fully explain your identifications.

Intended to be easy.

The aluminum ion, exhibiting a +3 charge, is clearly electron deficient – that's what positive charges mean, after all. It is therefore the Lewis acid. This means that the water molecules must be the Lewis acids – but which part of the water molecules in particular? The lone-pairs on the oxygen atoms. Lone pairs are electrons, and as such, are "electron rich" and "electron-pair donors" by definition.

12. (10 points) The following reactions have the equilibrium constants indicated at 1100 °C.

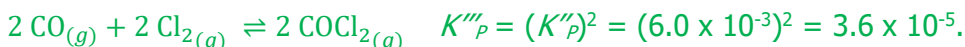


Write and *balance* (!! ) the equation for the overall reaction between  $\text{C}_{(s)}$ ,  $\text{CO}_{2(g)}$ , and  $\text{Cl}_{2(g)}$  to afford  $\text{COCl}_{2(g)}$ , and compute the equilibrium constant. (*Hint: You will need to manipulate the second chemical equation and its equilibrium constant.*) Show your work.

Intended to be difficult: you are required to determine how the equilibrium constant for the second reaction will change when you double the stoichiometric coefficients in it.

Notice that two  $\text{CO}_{(g)}$  are produced in the first reaction, but only one  $\text{CO}_{(g)}$  occurs in the second. Therefore, the second reaction must be doubled before it is added to the first, otherwise, the overall equation will not be balanced and the  $\text{CO}_{(g)}$  terms will not cancel. Note that multiplying the second equation by 2 requires squaring its equilibrium constant. Prove this to yourself if it is not obvious; it is the trick to answering this question correctly.

Therefore, compute the overall reaction and equilibrium constant when these two equations are added:



Overall reaction:



$$K_p = 4.7 \times 10^9$$

13. (10 points) Hydrogen gas and iodine gas react to form hydrogen iodide gas. Determine the initial and equilibrium concentrations of HI if the initial concentrations of  $\text{H}_2$  and  $\text{I}_2$  are both 0.16 M and their equilibrium concentrations are both 0.072 M. The equilibrium constant for the reaction is 54.2. (*Hint: write the balanced equation.*)

Intended to be medium - hard, partly because of the algebra, partly because the ICE table construction is unusual.

The balanced equation is:



An ICE table provides:

	$[\text{H}_2]$ (M)	$[\text{I}_2]$ (M)	$[\text{HI}]$ (M)
Initial	0.16	0.16	x
Change	-0.088	-0.088	2 (0.088)
Equilibrium	0.072	0.072	x + 2 (0.088)

from which the equilibrium expression:

$$\frac{(x + 2 (0.088))^2}{(0.072)^2} = 54.2$$

may be constructed.

Rearranging into standard form provides:

$$x^2 + 0.352 x - 0.2499 = 0$$

And the quadratic formula provides:

$$x = 0.353 \text{ M}$$

as the initial concentration. The equilibrium concentration will then be:

$$0.353 + 2 (0.088) = 0.529 \text{ M}$$

Alternatively, one may compute the equilibrium concentration by simply solving for  $[\text{HI}]$  in the equilibrium expression and using the equilibrium concentrations of the other species:

$$\frac{x^2}{0.072^2} = 54.2$$

Which provides  $x = 0.530 \text{ M}$ . Subtracting 2 (0.088) then provides the initial concentration. Either of these methods is acceptable.

### Bonus Questions

The ion product ( $K_w$ ) for water is  $1.0 \times 10^{-14}$  at 25 °C and  $3.8 \times 10^{-14}$  at 40 °C. Is the dissociation reaction endothermic or exothermic? Justify your conclusion.

Intended to be easy.

The equilibrium constant gets larger as the temperature goes up, indicating that when heat is added to the reaction, it goes further. This indicates that the reaction is endothermic.