(a)

$$CO_2(g) + H_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

When  $H_2(g)$  is mixed with  $CO_2(g)$  at 2,000 K, equilibrium is achieved according to the equation above. In one experiment, the following equilibrium concentrations were measured.

[H2] = 0.20 mol/L [CO2] = 0.30 mol/L [H2O] = [CO] = 0.55 mol/L What is the mole fraction of CO(q) in the equilibrium mixture?

(b) Using the equilibrium concentrations given above, calculate the value of *Kc*, the equilibrium constant for the reaction.

(c) i) Determine *Kp* in terms of *Kc* for this system.

ii) Using Kp from (i), what would be Kp' for the following rxn?

$$2 H2O (g) + 2 CO (g) \rightleftharpoons 2 CO2 (g) + 2 H2 (g)$$

- (d) When the system is cooled from 2,000 K to a lower temperature, 30.0 percent of the CO(g) is converted back to  $CO_2(g)$ . Calculate the value of Kc at this lower temperature.
- (e) In a different experiment, 0.50 mole of  $H_2(g)$  is mixed with 0.50 mole of  $CO_2(g)$  in a 3.0-liter reaction vessel at 2,000 K. Calculate the equilibrium concentration, in moles per liter, of CO(g) at this temperature.

2. 1998 D 
$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$
  $\Delta H^c = +131 \text{kJ}$ 

A rigid container holds a mixture of graphite pellets (C(s)),  $H_2O(g)$ , CO(g), and  $H_2(g)$  at equilibrium. State whether the number of moles of CO(g) in the container will <u>increase</u>, <u>decrease</u>, or <u>remain the same</u> after each of the following disturbances is applied to the original mixture. Explain each answer with a short statement.

Practice Quiz Equilibrium AP Chemistry
1. 1995 A

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- (a) Additional  $H_2(g)$  is added to the equilibrium mixture at constant volume.
- (b) The temperature of the equilibrium mixture is increased at constant volume.
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### 1997 A

The overall dissociation of oxalic acid, H2C2O4, is represented below. The overall dissociation constant is also indicated.

$$H_2C_2O_4 \rightleftharpoons 2 H^+ + C_2O_4^{2-}$$
  $K = 3.78 \times 10^{-6}$ 

- (a) What volume of 0.400-molar NaOH is required to neutralize completely a  $5.00 \times 10^{-3}$ -mole sample of pure oxalic acid?
- (b) Give the equations representing the first and second dissociations of oxalic acid. Calculate the value of the first dissociation constant,  $K_1$ , for oxalic acid if the value of the second dissociation constant,  $K_2$ , is 6.40 x 10<sup>-5</sup>.

[acid/base equilibrium chemistry starts here]

- (c) To a 0.015 molar solution of oxalic acid, a strong acid is added until the pH is 0.5. Calculate the  $[C2O4^{2-}]$  in the resulting solution. (Assume the change in volume is negligible.)
- (d) i) Calculate the value of the equilibrium constant, *Kb*, for the reaction that occurs when solid Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> is dissolved in water.
  - ii) Write a HYDROLYSIS reaction for the salt, Na2C2O4.

## STUDY YOUR SYLLABUS!!

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## STUDY YOUR SYLLABUS!!

# PRACTICE QUIZ/EQUILIBRIUM ANSWERS:

1995 A\_

A) 
$$0.55 + 0.55 + 0.30 + .20 = 1.6 \text{mol L}^{-1}$$
 CO =  $0.55 \text{ mol L}^{-1}$ 

$$.55/1.6 = 0.34 = X_{CO}$$

B) 
$$Kc = [CO][H2O] = [.55][.55] = Kc = 5.0$$
  
 $[CO2][H2] [.30][.20]$ 

C) (i) 
$$Kp = Kc(RT)^{\Delta n}$$
  $\Delta n = o$  So,  $Kp = Kc = 5.0$ 

(ii) The reaction was reversed and all of the coefficients were doubled.  $Kp' = 1/(Kp)^2$ 

О

Х

D) 
$$.55(.30) = 0.165 \rightarrow 0.17 \text{ mol}L^{-1} \text{ lost}$$

$$0.55 - 0.17 = 0.38 \text{ mol CO and H2O/L}$$

 $\rightarrow$  Since all chemicals are in 1:1 ratio, 0.17 mol/L of CO2 and H2O will be gained.

$$0.30 + 0.17 = 0.47 = [CO_2]$$
  
 $0.20 + 0.17 = 0.37 = [H_2]$ 

$$Kc = [CO][H2O] = [.38][.38] = 0.83 \text{ shifts left!}$$
  
 $[CO2][H2] [.47][.37]$ 

$$Kc = \frac{x^2}{(0.17 - x)^2} = 5.0$$

$$\sqrt{(x^2/(0.17 - x)^2)} = \sqrt{(5.0)}$$

$$X/(0.17 - X) = 2.2$$

[CO] = 
$$x = 0.38 - 2.2x \rightarrow 3.2x = 0.38 \rightarrow$$

$$3.2x = 0.38$$

$$[CO] = x = 0.38/3.2 = 0.12$$

<u> 1998 D</u>

heat + C + H<sub>2</sub>O 
$$\rightleftharpoons$$
 CO + H<sub>2</sub>

- A) Q > K, the reaction will shift left  $\propto$  [CO]  $\downarrow$ .
- B) Endothermic reactions will shift right when heat is added  $\propto \lceil CO \rceil \uparrow$ .
- C)  $\downarrow$  V  $\propto$   $\uparrow$  P The reaction will shift to the side with the least moles (coefficients) of gas. The reaction will shift left  $\propto \lceil CO \rceil \downarrow$ .
- D) Pulverizing the carbon pellets will increase the surface area  $\propto \uparrow$  rate. This does not affect K (the equilibrium constant). No  $\Delta$  in [CO].

1997 A

A) 
$$5.00 \times 10^{-3}$$
 mol acid  $\times 2 \text{ mol OH}^- = 0.400 \text{ mol OH}^-/\text{L}$   
1 mol oxalic

 $0.0100 \text{ mol OH}^{-} = .400 \text{ mol OH}^{-}/L \times Z \text{ liters}$ 

Z liters = .0100/.400 = .0250 L OR 25.0 mL.

B) 
$$Ka_{total} = Ka_1 \times Ka_2$$

$$3.78 \times 10^{-6} = \text{Ka}_1 \times 6.40 \times 10^{-5}$$

$$Ka_1 = 3.78 \times 10^{-6}$$
  
6.40 × 10<sup>-5</sup>

 $Ka_1 = 5.91 \times 10^{-2}$ 

C) pH = 0.5 So, 
$$-\log[H^+] = 0.5$$
  $\rightarrow$   $10^{-0.5} = [H^+] = 0.32M$ 

Remember that strong acid was added until the pH was 0.5, or the molarity reached 0.32 for [H<sup>+</sup>] at equilibrium. Substitute 0.32 into the ice table.

$$Ka_{total} = [H^{+}]^{2}[C_{2}O_{4}^{2^{-}}] = (0.32)^{2}x = 3.78 \times 10^{-6}$$
  
 $[H_{2}C_{2}O_{4}]$  .015 - x

$$(0.32)^{2}X = 3.78 \times 10^{-6} \rightarrow 0.10X = 5.7 \times 10^{-8} - 3.78 \times 10^{-6} \times 0.015 - X$$
  
 $0.015 - X$ 

$$0.10X = 5.7 \times 10^{-8} - 3.78 \times 10^{-6} \times 0.10X = 5.7 \times 10^{-8}$$

$$\rightarrow$$
 x = [C<sub>2</sub>O<sub>4</sub><sup>2-</sup>] = 5.7 x 10<sup>-7</sup>

Check to see if it's correct:

[H2C2O4] = 
$$0.015 - 5.7 \times 10^{-7} = 0.015$$
  
[H<sup>+</sup>] =  $0.32$   $\rightarrow$   $(.32)^2(5.7 \times 10^{-7}) = 3.9 \times 10^{-6}$  [pretty close!]  
[C2O4<sup>2-</sup>] =  $5.7 \times 10^{-7}$  0.015

D) I'll do (ii) first:

 $Na_2C_2O_4$  will dissociate into this  $\rightarrow 2Na^+ + C_2O_4^{2-}$  It is the oxalate ion that is the conjugate base of the weak acid, oxalic acid. Therefore, the conjugate base will act as a base in an aqueous solution – leading to hydrolysis.

"Hydro" referring to water . . . . . "Lysis" referring to splitting.

 $C_2O_4^{2-} + H_2O \rightleftharpoons HC_2O_4^{-} + OH^{-}$  (water's H was used to neutralize the conjugate base, resulting in free OH ions – a basic solution.)

(i) the Kb for the hydrolysis reaction above is:

Kb =  $[HC_2O_4][OH]$  notice that the H2O is not present in the expression due to it being a pure (I) [C<sub>2</sub>O<sub>4</sub><sup>2</sup>-]

$$Kw = Ka \times Kb = [OH^{-}][H^{+}]$$

$$Kb = Kw/Ka_2$$

$$Kb = Kw/Ka_2$$
 1.0 x 10<sup>-14</sup>/6.4 x 10<sup>-5</sup> \* = Kb

\* This value was revealed in part B.

$$Kb = 1.6 \times 10^{-10}$$

It must be based off of Ka, because

The expression contains both the acid and the base in question.

Proof:

$$HC_2O_4^- \rightleftarrows H^+ + C_2O_4^{2^-}$$
 If Kw = Ka x Kb and Ka2 =  $[H^+][C_2O_4^{2^-}]$  [ $HC_2O_4^-$ ]

and Kb = 
$$[HC_2O_4][OH]$$
 Then Kw =  $[H^+][C_2O_4][HC_2O_4][OH]$  =  $[OH][H^+]$  proof!  $[C_2O_4][C_2O_4]$ 

Also: If Kw =  $1.0 \times 10^{-14}$  = Ka2 x Kb. Then  $(6.4 \times 10^{-5})(1.6 \times 10^{-10})$  =  $1.0 \times 10^{-14}$  double proof!