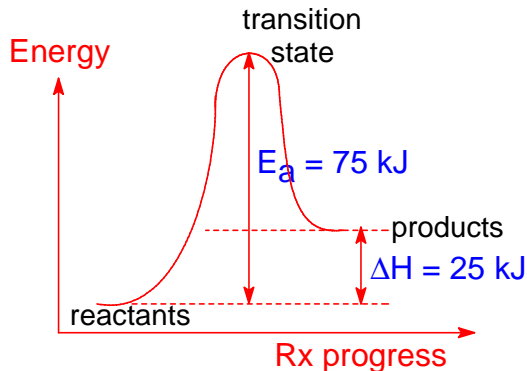


1. (7 points) Suppose that a simple reaction ( $A \longrightarrow$  products) has  $\Delta H^\circ = 25 \text{ kJ/mole}$  and  $E_a = 75 \text{ kJ/mole}$ . *Sketch and clearly label a reaction coordinate diagram* for this reaction. Draw a second diagram showing the effect of adding a catalyst.



With a catalyst,  $E_a$  gets smaller (lower transition state energy) but  $\Delta H$  stays the same.

2. (4 points) Circle any of the following that behave as weak acids in aqueous solution.

**H**OBr    HNO<sub>3</sub>    **H**F    **H**NO<sub>2</sub>    HONH<sub>2</sub>    **H**<sub>2</sub>SeO<sub>3</sub>    H<sub>2</sub>SO<sub>4</sub>    HBr

3. (2 points) In its aqueous solution chemistry, which of the following could best be used to illustrate the concept of an *amphoteric* substance? *Circle one.*

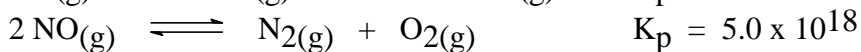
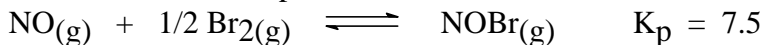
NH<sub>4</sub>Cl    **K**HCO<sub>3</sub>    Ba(OH)<sub>2</sub>    NaNO<sub>3</sub>    HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>

4. (4 points) The conjugate base of H<sub>2</sub>CF<sub>2</sub> is **HCF<sub>2</sub><sup>-</sup>**  
The conjugate acid of HAsO<sub>3</sub><sup>2-</sup> is **H<sub>2</sub>AsO<sub>3</sub><sup>-</sup>**

5. (2 points) Among the following, circle the *weakest* Brønsted-Lowry acid.

H<sub>2</sub>Se    **S**iH<sub>4</sub>    PH<sub>3</sub>    GeH<sub>4</sub>    H<sub>2</sub>S    AsH<sub>3</sub>

6. (8 points) **SHOW ALL WORK.** Consider these two reactions and their respective equilibrium constants ( $K_p$ ) at 300 °C. (+ 273 = 573 K)



Determine the concentration-based equilibrium constant ( $K_c$ ) for the following reaction at 300 °C.

$$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2 \text{NOBr(g)}$$

Multiply first equation by 2 (square  $K_p$ ), reverse second equation (invert  $K_p$ ), then add the equations (multiply the  $K$ 's) to get the overall reaction.

$$K_p = (7.5)^2 / (5.0 \times 10^{18}) = 1.125 \times 10^{-17}$$

$$K_p = K_c (RT)^{\Delta n}$$

$$\Delta n = \text{moles gas products} - \text{moles gas reactants} = 2 - 3 = -1$$

$$K_c = K_p / (RT)^{\Delta n} = (1.125 \times 10^{-17} / \text{atm}) / [(0.0821 \text{ L}\cdot\text{atm}/\text{mole}\cdot\text{K})(573 \text{ K})]^{-1}$$

$$K_c = 5.3 \times 10^{-16} \text{ L/mole} \quad (\text{or simply, } 5.3 \times 10^{-16})$$

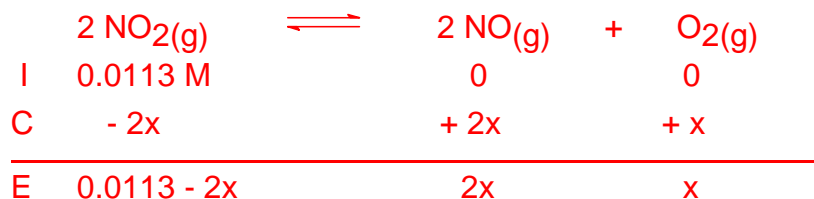
7. (10 points) **SHOW ALL WORK.** A sample of  $\text{NO}_2$  gas is heated to  $327^\circ\text{C}$  at which point it decomposes partially according to the following equation. When equilibrium is established, the gas mixture has a total pressure of 570 torr (1 atm/760 torr = 0.75 atm) and a density of 0.520 g/L. Determine  $K_C$  for this reaction at  $327^\circ\text{C}$ . (+ 273 = 600 K)



In 1.00 L, initial moles of  $\text{NO}_2 = (0.520 \text{ g}) (1 \text{ mole} / 46.0 \text{ g}) = 0.0113 \text{ moles}$

At equilibrium, total moles of gas:  $n = PV/RT$

$$n = (0.750 \text{ atm}) (1.00 \text{ L}) / (0.0821 \text{ L}\cdot\text{atm}/\text{mole}\cdot\text{K}) (600 \text{ K}) = 0.0152 \text{ moles}$$



$$\text{total moles} = 0.0152 = (0.0113 - 2x) + 2x + x = 0.0113 + x$$

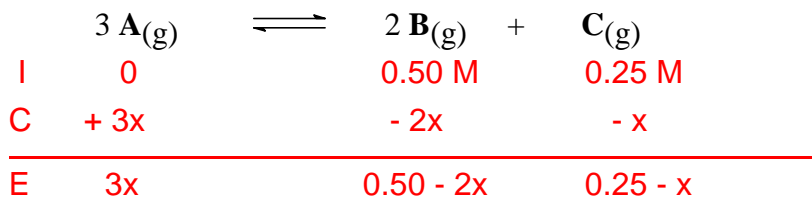
$$x = 0.0039$$

$$K_C = [\text{NO}]^2 [\text{O}_2] / [\text{NO}_2]^2 = (2x)^2 (x) / (0.0113 - 2x)^2$$

plug in  $x = 0.0039$ :

$$K_C = (0.0078)^2 (0.0039) / (0.0113 - 0.0078)^2 = 0.019$$

8. (10 points) **SHOW ALL WORK.** At  $400^\circ\text{C}$ ,  $K_C = 2.50 \times 10^8$  for the following reaction. At this temperature, 0.50 moles of **B** and 0.25 moles of **C** are combined in a 1.00-L container and the system is allowed to reach equilibrium. Determine the equilibrium concentration of **A**. (Clearly state and justify any assumptions that you make.)



$$K_C = 2.50 \times 10^8 = [\text{B}]^2 [\text{C}] / [\text{A}]^3 = (0.50 - 2x)^2 (0.25 - x) / (3x)^3$$

Since  $K_C$  is very large, the reaction is essentially complete at equilibrium. Thus,  $[\text{A}]$  should be very small, so assume  $2x \ll 0.50$  and  $x \ll 0.25$ .

$$2.50 \times 10^8 \sim (0.50)^2 (0.25) / (3x)^3$$

$$x \sim 2.1 \times 10^{-4} \text{ M} \quad (\text{assumption is OK!})$$

$$[\text{A}] = 3x \sim 6.3 \times 10^{-4} \text{ M}$$

9. (a) (5 points) Determine the pH of each of the following solutions.

Solution A: 600 mL of 0.0125 M HClO<sub>4</sub>      pH = 1.90

Solution B: 400 mL of 0.0250 M KOH      pH = 12.40

- (b) (8 points) **SHOW ALL WORK.** Now suppose that solutions A and B are mixed together. Determine the pH of the final solution. Your method must include an appropriate *net ionic equation*.

moles HClO<sub>4</sub> = (0.600 L) (0.0125 mole/L) = 0.00750 moles

moles KOH = (0.400 L) (0.0250 mole/L) = 0.0100 moles

net ionic equation: H<sup>+</sup> + OH<sup>-</sup> → H<sub>2</sub>O

1 mole H<sup>+</sup> neutralizes 1 mole OH<sup>-</sup>

excess OH<sup>-</sup> = 0.0100 - 0.00750 = 0.00250 moles

total volume = 400 mL + 600 mL = 1,000 mL = 1.00 L

[OH<sup>-</sup>] = 0.00250 mole/L      pOH = -log (0.00250) = 2.60

pH = 14.00 - pOH = 11.40

10. A 0.15 M solution of formic acid, HCO<sub>2</sub>H, is found to have a pH of 2.29.

- (a) (3 points) Write a *balanced chemical equation for the major equilibrium reaction* that is occurring in an aqueous solution of HCO<sub>2</sub>H.



- (b) (7 points) **SHOW ALL WORK.** Determine the pK<sub>a</sub> value of HCO<sub>2</sub>H.

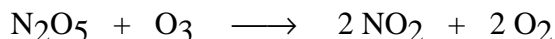
$$K_a = [\text{H}^+][\text{HCO}_2^-] / [\text{HCO}_2\text{H}]$$

$$[\text{H}^+] = [\text{HCO}_2^-] = 10^{-2.29} = 5.13 \times 10^{-3} \text{ M}$$

$$K_a \sim (5.13 \times 10^{-3})^2 / (0.15) \sim 1.75 \times 10^{-4}$$

$$\text{p}K_a = -\log K_a = -\log (1.75 \times 10^{-4}) = 3.76$$

11. The experimental rate law for the following reaction is found to be: rate = k[N<sub>2</sub>O<sub>5</sub>].



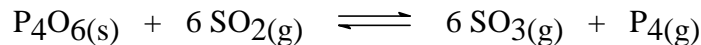
- (a) (3 points) *In 25 words or less, explain* why this reaction cannot occur by a one-step mechanism. **Since the rate does not depend on [O<sub>3</sub>], O<sub>3</sub> cannot be a reactant in the slow step. Therefore more than one step is required.**

- (b) (7 points) *Propose* a reasonable *two-step mechanism* for this reaction that is consistent with the experimental rate law. Clearly indicate which step in your mechanism is the rate-determining step. If your proposed mechanism contains an intermediate, circle it.



predicted rate law (based on slow step): rate = k[N<sub>2</sub>O<sub>5</sub>]

12. Consider the following heterogeneous equilibrium reaction at 500 K.



(a) (3 points) Write the equilibrium expression for this reaction.

$$K_c = [\text{SO}_3]^6 [\text{P}_4] / [\text{SO}_2]^6$$

(b) (5 points) How will the equilibrium concentration of  $\text{P}_4(\text{g})$  be affected by each of following changes? Indicate your answer by writing the appropriate letter.

[I = increase, D = decrease, N = no change]

Change	[P <sub>4</sub> ]
remove some SO <sub>2</sub> (g)	D
add some P <sub>4</sub> O <sub>6</sub> (s)	N
decrease the pressure	I
add a catalyst	N

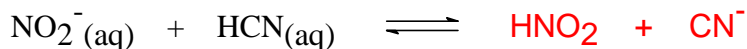
(c) (2 points) The above reaction is known to be endothermic. If the temperature is increased, then the value of  $K_c$  will do which of the following? **Circle one.**

increase

decrease

not change

13. (10 points) Using acid-base concepts, predict the logical products of the following reaction in aqueous solution. Write **Lewis electron dot formulas** (including formal charges and/or resonance forms if needed) for all reactants and products. *Clearly indicate which reactant is the Lewis acid and which is the Lewis base.* Use arrow(s) to illustrate the formation and breaking of any bonds as the reaction proceeds from left to right.



Lewis base

