Name _____ AP Chemistry ___/___/___

Chapter 13 Collected AP Exam Free Response Questions 1980 – 2010 Answers

1980 - #6

$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$ $\Delta H = +42.1$ kilocalories

Suppose the substances in the reaction above are at equilibrium at 600 K in volume V and at pressure P. State whether the partial pressure of $NH_3(g)$ will have increased, decreased, or remained the same when equilibrium is reestablished after each of the following disturbances of the original system. Some solid NH_4Cl remains in the flask at all times. Justify each answer with a one- or two-sentence explanation.

(a) A small quantity of NH_4Cl is added. **Same - Solid has constant concentration (activity is unity): therefore, no equilibrium shift.**

(b) The temperature of the system is increased. **Increased - Reaction shifts in favor of gases because reaction is endothermic.**

(c) The volume of the system is increased. **Same - As volume increases, reaction is driven to the right, producing NH_3 and HCl so as to yield same partial pressure of each gas at the new equilibrium.**

(d) A quantity of gaseous HCl is added. **Decreased - Reaction shifts left to relieve stress of added HCl, consuming NH_3 and reducing its partial pressure.**

(e) A quantity of gaseous NH_3 is added. **Increased - Added NH_3 causes equilibrium shift in favor of solid NH_4Cl; however, only part of the added NH_3 reacts so that P_{NH3} will be greater than the original.**

1981 - #1

Ammonia hydrogen sulfide is a crystalline solid that decomposes as follows:

$NH_4HS(s) \rightarrow NH_3(g) + H_2S(g)$

(a) Some solid NH_4HS is placed in an evacuated vessel at 25°C. After equilibrium is attained, the total pressure inside the vessel is found to be 0.659 atmosphere. Some solid NH_4HS remains in the vessel at equilibrium. For this decomposition, write the expression for K_p and calculate its numerical value at 25°C. **$K_p = (P_{NH3})(P_{H2S})$ 0.109 atm^2**

(b) Some extra NH_3 gas is injected into the vessel containing the sample described in part (a). When equilibrium is reestablished at 25°C, the partial pressure of NH_3 is twice the partial pressure of H_2S. Calculate the numerical value of the partial pressure of NH_3 and the partial pressure of H_2S in the vessel after the NH_3 has been added and equilibrium has been reestablished. **0.233 atm = P_{H2S}, 0.466 atm = P_{NH3}**

(c) In a different experiment, NH_3 gas and H_2S gas are introduced into an empty 1.00-liter vessel at 25°C. The initial partial pressure of each gas is 0.500 atmosphere. Calculate the number of moles of solid NH_4HS that is present when equilibrium is established. **6.95×10^{-3} moles**

1981 - #9c & d

$PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$

For the reaction above, $\Delta H° = +22.1$ kilocalories per mole at 25°C.

(c) State whether an increase in temperature drives this reaction to the right, to the left, or has no effect. Explain. **Right, products are favored. For the system at constant pressure: absorption of heat favors the products. An argument using LeChâtelier's principle can be used with heat considered as a reactant.**

(d) State whether a decrease in the volume of the system at constant temperature drives this reaction to the right, to the left, or has no effect. Explain. **Left, the reactant is favored. A decrease in the volume would increase the pressure and the strain is relieved by the reverse reaction which produces 1 mole of gas from 2 moles of gas.**

1983 - #1

Sulfuryl chloride, SO_2Cl_2, is a highly reactive gaseous compound. When heated, it decomposes as follows.

$SO_2Cl_2(g) <===> SO_2(g) + Cl_2(g)$

This decomposition is endothermic. A sample of 3.509 grams of SO_2Cl_2 is placed in an evacuated 1.00-liter bulb and the temperature is raised to 375 K.

(a) What would be the pressure in atmospheres in the bulb if no dissociation of the $SO_2Cl_2(g)$ occurred? **P = 0.800 atm**

(b) When the system has come to equilibrium at 375 K, the total pressure in the bulb is found to be 1.43 atmospheres. Calculate the partial pressures of SO_2, Cl_2, and SO_2Cl_2 at equilibrium at 375 K. **$P_{SO2} = P_{Cl2} = 0.63$ atm; $P_{SO2Cl2} = 0.17$ atm**

www.sarep.com

(c) Give the expression for the equilibrium constant (either K_p or K_c) for the decomposition of $SO_2Cl_2(g)$ at 375 K. Calculate the value of the equilibrium constant you have given, and specify its units. **K_p = 2.3 atm, K_c= 0.076**
(d) If the temperature were raised to 500 K, what effect would this have on the equilibrium constant? Explain briefly. **An endothermic process absorbs heat during dissociation so $K_{500} > K_{375}$ or a stress is placed upon the system and K increases in order to remove the stress.**

1988 - #1
At elevated temperatures, $SbCl_5$ gas decomposes into $SbCl_3$ gas and Cl_2 gas, as shown by the following equation.
$SbCl_5$ <===> $SbCl_3 + Cl_2$
(a) An 89.7-gram sample of $SbCl_5$ (molecular weight 299.0) is placed in an evacuated 15.0-liter container at 182°C.
(i) What is the concentration in moles per liter of $SbCl_5$ in the container before any decomposition occurs? **0.020 M**
(ii) What is the pressure in atmospheres of $SbCl_5$ in the container before any decomposition occurs? **0.747 atm**
(b) If the $SbCl_5$ is 29.2 percent decomposed when equilibrium is established at 182°C, calculate the value for either equilibrium constant, K_p or K_c, for this decomposition reaction. Indicate whether you are calculating K_p or K_c.
$K_c = 2.41 \times 10^{-3}$, $K_p = 8.98 \times 10^{-2}$
(c) In order to produce some $SbCl_5$, a 1.00-mole sample of $SbCl_3$ is first placed in an empty 2.00-liter container maintained at a temperature different from 182°C. At this temperature K_c equals 0.117. How many moles of Cl_2 must be added to this container to reduce the number of moles of $SbCl_3$ to 0.700 mole at equilibrium? **Moles Cl_2 that must be added = 0.40 mol**

1988 - #6
$NH_4HS(s)$ <===> $NH_3(g) + H_2S(g)$
For this reaction, $\Delta H° = +93$ kilojoules
The equilibrium above is established by placing solid NH_4HS in an evacuated container at 25°C. At equilibrium, some solid NH_4HS remains in the container. Predict and explain each of the following.
(a) The effect on the equilibrium partial pressure of NH_3 gas when additional solid NH_4HS is introduced into the container. **The equilibrium pressure of NH_3 gas would be unaffected $K_p = (P_{NH3})(P_{H2S})$. Thus the amount of solid NH_4HS present does not affect the equilibrium.**
(b) The effect on the equilibrium partial pressure of NH_3 gas when additional H_2S gas is introduced into the container. **The equilibrium pressure of NH_3 gas would decrease. In order for the pressure equilibrium constant, K_p, to remain constant, the equilibrium pressure of NH_3 must decrease when the pressure of H_2S is increased. $K_p = (P_{NH3})(P_{H2S})$**
(c) The effect on the mass of solid NH_4HS present when the volume of the container is decreased. **The mass of NH_4HS increases. A decrease in volume causes the pressure of each gas to increase. To maintain the value of the pressure equilibrium constant, K_p, the pressure of each of the gases must decrease. That decrease realized by the formation of more solid NH_4HS.**
(d) The effect on the mass of solid NH_4HS present when the temperature is increased.
The mass of NH_4HS decreases because the endothermic reaction absorbs heat and goes nearer to completion (to the right) as the temperature increases.

1992 - #1
$2\ NaHCO_3(s)$ <===> $Na_2CO_3(s) + H_2O(g) + CO_2(g)$
Solid sodium hydrogen carbonate, $NaHCO_3$, decomposes on heating according to the equation above.
(a) A sample of 100. grams of solid $NaHCO_3$ was placed in a previously evacuated rigid 5.00-liter container and heated to 160. °C. Some of the original solid remained and the total pressure in the container was 7.76 atmospheres when equilibrium was reached. Calculate the number of moles of H_2O (g) present at equilibrium. **0.545 mol**
(b) How many grams of the original solid remained in the container under the conditions described in (a)?
8.4 g of $NaHCO_3$ remaining
(c) Write the equilibrium expression for the equilibrium constant, K_p, and calculate its value for the reaction under the conditions in (a). **$K_p = (P_{H2O})(P_{CO2})$; $K_p = 15.1\ atm^2$**
(d) If 110. grams of solid $NaHCO_3$ had been placed in the 5.00-liter container and heated to 160 °C, what would the total pressure have been at equilibrium? Explain. **The total pressure would remain at 7.76 atm. Since some solid remained when 100. g was used (and there had been no temperature change), then using 110 g would not affect the equilibrium.**

www.sahep.com

1995 - #1

$H_2(g) + CO_2(g) <===> H_2O(g) + CO(g)$

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.
$[H_2] = 0.20$ mol/L
$[CO_2] = 0.30$ mol/L
$[H_2O] = [CO] = 0.55$ mol/L
(a) What is the mole fraction of CO(g) in the equilibrium mixture? **0.34**
(b) Using the equilibrium concentrations given above, calculate the value of K_c, the equilibrium constant for the reaction. **5.0**
(c) Determine K_p, in terms of K_c for this system. **$K_p = 5.0$**
(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 K_c at this lower temperature. **0.92**
(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. **0.11 mol/L**

1997 - #7 c & d

For the gaseous equilibrium represented below, it is observed that greater amounts of PCl_3 and Cl_2 are produced as the temperature is increased.

$PCl_5(g) <===> PCl_3(g) + Cl_2(g)$

(c) If He gas is added to the original reaction mixture at constant volume and temperature, what will happen to the partial pressure of Cl_2? Explain. **no change; P_{He} is not part of the reaction (He is not involved)**
(d) If the volume of the original reaction is decreased at constant temperature to half the original volume, what will happen to the number of moles of Cl_2 in the reaction vessel? Explain. **moles of Cl_2 will decrease**
The decrease in volume leads to an increase in pressure (concentration), therefore the reaction shifts to the left because Q > Kc, or the reaction shifts toward the lesser moles of gas.

1998 - #7

$C(s) + H_2O(g) <===> CO(g) + H_2(g) \quad \Delta H° = +131$ 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 increase, decrease, or remain the same after each of the following disturbances is applied to the original mixture. For each case, assume that all other variables remain constant except for the given disturbance. Explain each answer with a short statement.
(a) Additional $H_2(g)$ is added to the equilibrium mixture at constant volume. **The number of moles of CO will decrease because adding H_2, will make the reaction shift to the left.**
(b) The temperature of the equilibrium mixture is increased at constant volume. **The number of moles of CO will increase because since the reaction is endothermic, adding of the heat (as a reactant) will drive the reaction to the right.**
(c) The volume of the container is decreased at constant temperature. **The number of moles of CO will decrease because there are more moles of gas (2) on the right than on the left (1), thus decreasing the volume which increases the pressure causes the reaction to shift to the left.**
(d) The graphite pellets are pulverized. **The number of moles of CO will stay the same because solids are not involved in the equilibrium expression**

2000 - #1

$2\ H_2S(g) \rightleftharpoons 2\ H_2(g) + S_2(g)$

When heated, hydrogen sulfide gas decomposes according to the equation above. A 3.40 g sample of $H_2S(g)$ is introduced into an evacuated rigid 1.25 L container. The sealed container is heated to 483 K, and 3.72×10^{-2} mol of $S_2(g)$ is present at equilibrium.
(a) Write the expression for the equilibrium constant, K_c, for the decomposition reaction represented above.

$$K_c = \frac{[H_2]^2[S_2]}{[H_2S]^2}$$

(b) Calculate the equilibrium concentration, in mol L^{-1}, of the following gases in the container at 483 K.
(i) $H_2(g)$ **5.95×10^{-2} *M***

www.sarter.com

(ii) $H_2S(g)$ **2.05×10^{-2} *M***

(c) Calculate the value of the equilibrium constant, K_c, for the decomposition reaction at 483 K. **0.250**

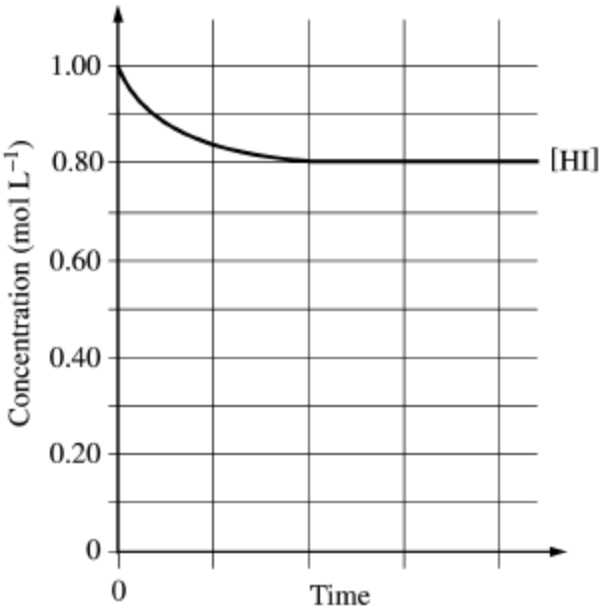
(d) Calculate the partial pressure of $S_2(g)$ in the container at equilibrium at 483 K. **1.18 atm**

(e) For the reaction $H_2(g) + \frac{1}{2}S_2(g) \rightleftharpoons H_2S(g)$ at 483 K, calculate the value of the equilibrium constant, K_c. **2.00**

2003B - #1

$2\ HI(g) \rightleftharpoons H_2(g) + I_2(g)$

After a 1.0 mole sample of HI(g) is placed into an evacuated 1.0 L container at 700. K, the reaction represented above occurs. The concentration of HI(g) as a function of time is shown below.



(a) Write the expression for the equilibrium constant, K_c, for the reaction.

$$K_c = \frac{[H_2][I_2]}{[HI]^2}$$

(b) What is [HI] at equilibrium? **0.80 M**

(c) Determine the equilibrium concentrations of $H_2(g)$ and $I_2(g)$. **$[I_2] = [H_2] = 0.10$ *M***

(d) On the graph above, make a sketch that shows how the concentration of $H_2(g)$ changes as a function of time. **The curve should have the following characteristics:**

- start at 0 *M*;

- increase to 0.1 *M*;

- reach equilibrium at the same time [HI] reaches equilibrium

(e) Calculate the value of the following equilibrium constants at 700. K.

(i) K_c **0.016**

(ii) K_p **0.016**

(f) At 1,000 K, the value of K_c for the reaction is 2.6×10^{-2}. In an experiment, 0.75 mole of HI(g), 0.10 mole of $H_2(g)$, and 0.50 mole of $I_2(g)$ are placed in a 1.0 L container and allowed to reach equilibrium at 1,000 K. Determine whether the equilibrium concentration of HI(g) will be greater than, equal to, or less than the initial concentration of HI(g). Justify your answer. **$Q = 8.9 \times 10^{-2}$** **$K_c = 2.6 \times 10\text{-}2$** **$Q > K_c$**

To establish equilibrium, the numerator must decrease and the denominator must increase. Therefore, [HI] will increase.

2004B - #1

$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$

For the reaction represented above, the value of the equilibrium constant, K_p, is 3.1×10^{-4} at 700. K.

(a) Write the expression for the equilibrium constant, K_p, for the reaction.

$$K_p = \frac{p^2_{NH_3}}{p_{N_2} \times p^3_{H_2}}$$

(b) Assume that the initial partial pressures of the gases are as follows:

$pN_2 = 0.411$ atm, $pH_2 = 0.903$ atm, and $pNH_3 = 0.224$ atm.

(i) Calculate the value of the reaction quotient, Q, at these initial conditions. **Q = 0.166**

(ii) Predict the direction in which the reaction will proceed at 700. K if the initial partial pressures are those given above. Justify your answer. **Since *Q* > *Kp* , the numerator must decrease and the denominator must increase, so the reaction must proceed from right to left to establish equilibrium.**

www.sar

(c) Calculate the value of the equilibrium constant, K_c, given that the value of K_p for the reaction at 700. K is 3.1×10^{-4}. **1.0 = *Kc***

(d) The value of K_p for the reaction represented below is 8.3×10^{-3} at 700. K.

$$NH_3(g) + H_2S(g) \rightleftharpoons NH_4HS(g)$$

Calculate the value of K_p at 700. K for each of the reactions represented below.

(i) $NH_4HS(g) \rightleftharpoons NH_3(g) + H_2S(g)$ **1.2×10^2**

(ii) $2\ H_2S(g) + N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_4HS(g)$ **2.1×10^{-8}**

2007B - #1

A sample of solid U_3O_8 is placed in a rigid 1.500 L flask. Chlorine gas, $Cl_2(g)$, is added, and the flask is heated to 862°C. The equation for the reaction that takes place and the equilibrium-constant expression for the reaction are given below.

$$U_3O_8(s) + 3Cl_2(g) \rightleftharpoons 3UO_2Cl_2(g) + O_2(g)$$

When the system is at equilibrium, the partial pressure of $Cl_2(g)$ is 1.007 atm and the partial pressure of $UO_2Cl_2(g)$ is 9.734×10^{-4} atm.

(a) Calculate the partial pressure of $O_2(g)$ at equilibrium at 862°C. **3.245×10^{-4} atm O_2**

(b) Calculate the value of the equilibrium constant, K_p, for the system at 862°C. **2.931×10^{-13}**

(f) After a certain period of time, 1.000 mol of $O_2(g)$ is added to the mixture in the flask. Does the mass of $U_3O_8(s)$ in the flask increase, decrease, or remain the same? Justify your answer. **Increase. The addition of O_2 will cause the reaction to shift left to relieve the stress and more U_3O_8 will be produced.**

2008 - #1

$$C(s) + CO_2(g) \rightleftharpoons 2\ CO(g)$$

Solid carbon and carbon dioxide gas at 1,160 K were placed in a rigid 2.00 L container, and the reaction represented above occurred. As the reaction proceeded, the total pressure in the container was monitored. When equilibrium was reached, there was still some C(*s*) remaining in the container. Results are recorded in the table below.

Time (hours)	Total Pressure of Gases in Container at 1,160 K (atm)
0.0	5.00
2.0	6.26
4.0	7.09
6.0	7.75
8.0	8.37
10.0	8.37

(a) Write the expression for the equilibrium constant, K_p, for the reaction.

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}}$$

(b) Calculate the number of moles of $CO_2(g)$ initially placed in the container. (Assume that the volume of the solid carbon is negligible.) **0.105 mol**

(c) For the reaction mixture at equilibrium at 1,160 K, the partial pressure of the $CO_2(g)$ is 1.63 atm. Calculate

(i) the partial pressure of $CO(g)$, and **6.74 atm**

(ii) the value of the equilibrium constant, K_p. **27.9**

(d) If a suitable solid catalyst were placed in the reaction vessel, would the final total pressure of the gases at equilibrium be greater than, less than, or equal to the final total pressure of the gases at equilibrium without the catalyst? Justify your answer. (Assume that the volume of the solid catalyst is negligible.)

In another experiment involving the same reaction, a rigid 2.00 L container initially contains 10.0 g of C(*s*) , plus $CO(g)$ and $CO_2(g)$, each at a partial pressure of 2.00 atm at 1,160 K.

The total pressure of the gases at equilibrium with a catalyst present would be equal to the total pressure of the gases without a catalyst. Although a catalyst would cause the system to reach the same equilibrium state

www.sartep.com

more quickly, it would not affect the extent of the reaction, which is determined by the value of the equilibrium constant, K_p.

(e) Predict whether the partial pressure of $CO_2(g)$ will increase, decrease, or remain the same as this system approaches equilibrium. Justify your prediction with a calculation. **Q = 2.00 atm; 2.00 < K_p (= 27.9); therefore CO_2 pressure will decrease as the system approaches equilibrium.**

2008B - #1

Answer the following questions regarding the decomposition of arsenic pentafluoride, $AsF_5(g)$.

(a) A 55.8 g sample of $AsF_5(g)$ is introduced into an evacuated 10.5 L container at 105°C.

(i) What is the initial molar concentration of $AsF_5(g)$ in the container? **0.0313 *M***

(ii) What is the initial pressure, in atmospheres, of the $AsF_5(g)$ in the container? **0.969 atm**

At 105°C, $AsF_5(g)$ decomposes into $AsF_3(g)$ and $F_2(g)$ according to the following chemical equation.

$AsF_5(g) \rightleftharpoons AsF_3(g) + F_2(g)$

(b) In terms of molar concentrations, write the equilibrium-constant expression for the decomposition of $AsF_5(g)$.

$$K = \frac{[AsF_3]\,[F_2]}{[AsF_5]}$$

(c) When equilibrium is established, 27.7 percent of the original number of moles of $AsF_5(g)$ has decomposed.

(i) Calculate the molar concentration of $AsF_5(g)$ at equilibrium. **0.0226 *M***

(ii) Using molar concentrations, calculate the value of the equilibrium constant, K_{eq} , at 105°C. **0.00333**

(d) Calculate the mole fraction of $F_2(g)$ in the container at equilibrium. **0.217**

2009 - #5 a,b & d

Reaction	Equation	ΔH°_{298}
X	$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$	+131 kJ mol^{-1}
Y	$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$	+41 kJ mol^{-1}

Answer the following questions using the information related to reactions X, Y, and Z in the table above.

(a) For reaction X, write the expression for the equilibrium constant, *Kp*.

$$K_p = \frac{p_{CO} \times p_{H_2}}{p_{H_2O}}$$

(b) For reaction X, will the equilibrium constant, *Kp* , increase, decrease, or remain the same if the temperature rises above 298 K ? Justify your answer.

***Kp* will increase.**

If the temperature is increased for an endothermic reaction (ΔH°_{298} = +131 kJ mol^{-1}), then by Le Chatelier's principle the reaction will shift toward products, thereby absorbing energy. With greater concentrations of products at equilibrium, the value of *Kp* will increase.

(d) For reaction Y at 298 K, which is larger: the total bond energy of the reactants or the total bond energy of the products? Explain.

The total bond energy of the reactants is larger.

Reaction Y is endothermic (ΔH_{298} = + 41 kJ mol^{-1} > 0), so there is a net input of energy as the reaction occurs. Thus, the total energy required to break the bonds in the reactants must be greater than the total energy released when the bonds are formed in the products.

www.sartep.com