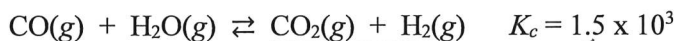


- 1) $\text{NH}_3(\text{g})$ was synthesized at 200°C in the presence of a powdered $\text{Os}(\text{s})$ catalyst, leading to the equilibrium system represented above. Which of the following changes would result in more $\text{NH}_3(\text{g})$ in the mixture after equilibrium is reestablished?

A) Replacing the powdered $\text{Os}(\text{s})$ with a solid cube of $\text{Os}(\text{s})$ of the same total mass (shift right) C) Removing some $\text{H}_2(\text{g})$
shift left shift left

B) Increasing the temperature of the system to 250°C at constant pressure

D) Adding some $\text{N}_2(\text{g})$



- 2) A 2.0 mol sample of $\text{CO}(\text{g})$ and a 2.0 mol sample of $\text{H}_2\text{O}(\text{g})$ are introduced into a previously evacuated 100. L rigid container, and the temperature is held constant as the reaction represented above reaches equilibrium. Which of the following is true at equilibrium?

A) $[\text{H}_2\text{O}] > [\text{CO}]$ and $[\text{CO}_2] > [\text{H}_2]$

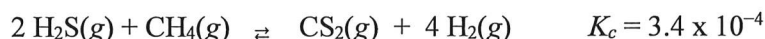
B) $[\text{H}_2\text{O}] > [\text{H}_2]$

C) $[\text{CO}_2] > [\text{CO}]$

D) $[\text{CO}] = [\text{H}_2\text{O}] = [\text{CO}_2] = [\text{H}_2]$

favored

equilibrium doesn't mean equal { }



- 3) A 0.10 mol sample of each of the four species in the reaction represented above is injected into a rigid, previously evacuated 1.0 L container. Which of the following species will have the highest concentration when the system reaches equilibrium?

A) $\text{H}_2\text{S}(\text{g})$

B) $\text{CH}_4(\text{g})$

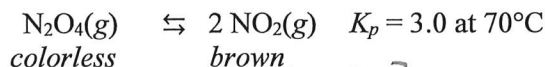
C) $\text{CS}_2(\text{g})$

D) $\text{H}_2(\text{g})$

2 mol vs 1 mol

Questions 4-7 refer to the following information.

A mixture of $\text{NO}_2(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$ is placed in a glass tube (sealed) and allowed to reach equilibrium at 70°C , as represented here:



- 4) If $P \text{N}_2\text{O}_4$ is 1.33 atm when the system is at equilibrium at 70°C , what is $P \text{NO}_2$?

A) 0.44 atm

B) 2.0 atm

C) 2.3 atm

D) 4.0 atm

$$K_p = \frac{(\text{NO}_2)^2}{(\text{N}_2\text{O}_4)}$$

$$3.0 = \frac{(2.0)^2}{1.33}$$

$\text{NO}_2 = 2.0$

- 5) Which of the following statements best helps to explain why the contents of the tube containing the equilibrium mixture turned a lighter color when the tube was placed into an ice bath?

A) The forward reaction is exothermic.

B) The forward reaction is endothermic.

C) The ice bath lowered the activation energy.

D) The ice bath raised the activation energy.

heat on left
rxn shifted left

- 6) Which of the following best predicts how the partial pressures of the reacting species will be affected if a small amount of $\text{Ar}(\text{g})$ is added to the equilibrium mixture at constant volume?

A) $P \text{NO}_2$ will decrease and $P \text{N}_2\text{O}_4$ will increase.

B) $P \text{NO}_2$ will increase and $P \text{N}_2\text{O}_4$ will decrease.

C) Both $P \text{NO}_2$ and $P \text{N}_2\text{O}_4$ will decrease.

D) No change will take place.

inert gas, doesn't affect equilibrium

- 7) Which of the following statements about ΔH° for the reaction is correct?

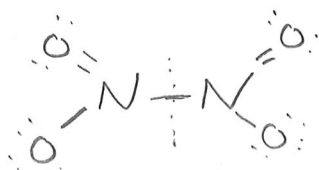
A) $\Delta H^\circ < 0$ because energy is released when the N-N bond breaks.

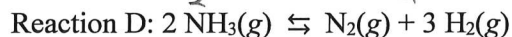
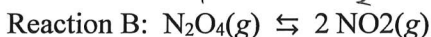
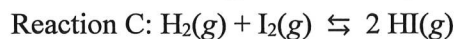
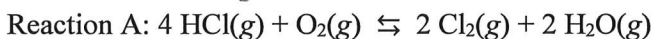
B) $\Delta H^\circ < 0$ because energy is required to break the N-N bond.

C) $\Delta H^\circ > 0$ because energy is released when the N-N bond breaks.

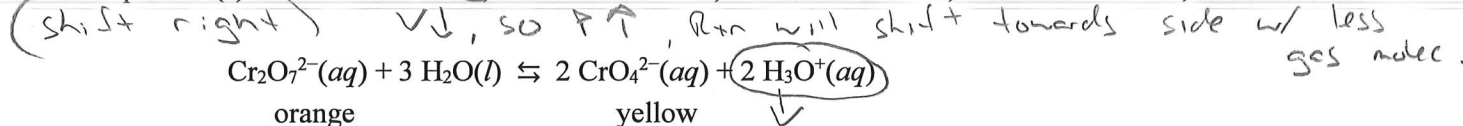
D) $\Delta H^\circ > 0$ because energy is required to break the N-N bond.

Endothermic





- 8) The reactions represented above are carried out in sealed, rigid containers and allowed to reach equilibrium. If the volume of each container is reduced from 1.0 L to 0.5 L at constant temperature, for which of the reactions will the amount of product(s) be increased?



- 9) The equilibrium system represented by the equation above initially contains equal concentrations of $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ and $\text{CrO}_4^{2-}(\text{aq})$. Which of the following statements correctly predicts the result of adding a sample of 6.0 M NaOH(aq) to the system, and provides an explanation?

- A) The mixture will become more orange because $\text{OH}^-(\text{aq})$ will oxidize the Cr in $\text{CrO}_4^{2-}(\text{aq})$.
 B) The mixture will become more yellow because $\text{OH}^-(\text{aq})$ will reduce the Cr in $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$.
 C) The mixture will become more yellow because $\text{OH}^-(\text{aq})$ will shift the equilibrium toward products. (neutralize acid)
 D) The color of the mixture will not change because $\text{OH}^-(\text{aq})$ does not appear in the equilibrium expression.



$$Q = \frac{[2.5]^2}{[0.150]^3} = 1.8 \times 10^3$$

- 10) For the system represented above, $[\text{O}_2]$ and $[\text{O}_3]$ initially are 0.150 mol/L and 2.5 mol/L respectively.

Which of the following best predicts what will occur as the system approaches equilibrium at 570 K?

- A) The amount of $\text{O}_3(\text{g})$ will increase, because $Q < K_c$.
 B) The amount of $\text{O}_3(\text{g})$ will decrease, because $Q < K_c$.
 C) The amount of $\text{O}_3(\text{g})$ will increase, because $Q > K_c$.
 D) The amount of $\text{O}_3(\text{g})$ will decrease, because $Q > K_c$. (rxn will shift left)

- 11) Based on the information in the table, which of the following expressions represents the equilibrium constant, K , for the reaction represented by the equation: $\text{La}^{3+} + \text{CO}_3^{2-} \rightleftharpoons \text{LaCO}_3^+$?

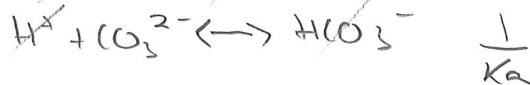
A) $K = (K_1)(K_a)(K_w)$

B) $K = \frac{(K_1)(K_a)}{K_w}$

C) $K = \frac{K_1}{(K_a)(K_w)}$

D) $K = \frac{(K_1)(K_w)}{K_a}$

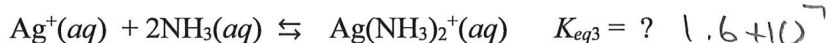
Reaction	K_{eq}
$\text{La}^{3+} + \text{OH}^- + \text{HCO}_3^- \rightleftharpoons \text{LaCO}_3^+ + \text{H}_2\text{O}$	K_1
$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$ (slip)	K_a
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	K_w



- 12) $\text{Ag}^+(\text{aq}) + \text{NH}_3(\text{aq}) \rightleftharpoons \text{Ag}(\text{NH}_3)^+(\text{aq}) \quad K_{eq1} = 2.0 \times 10^3$
 $\text{Ag}(\text{NH}_3)^+(\text{aq}) + \text{NH}_3(\text{aq}) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(\text{aq}) \quad K_{eq2} = 8.0 \times 10^3$

$$K_{eq1} \cdot K_{eq2} = K_{eq3}$$

Equal volumes of 0.1 M $\text{AgNO}_3(\text{aq})$ and 2.0 M $\text{NH}_3(\text{aq})$ are mixed and the reactions represented above occur. Which Ag species will have the highest concentration in the equilibrium system shown below, and why?



Right side FAVORED

- A) $\text{Ag}^+(\text{aq})$, because $K_{eq3} = 4$

- B) $\text{Ag}^+(\text{aq})$, because $K_{eq1} < K_{eq2}$

- C) $\text{Ag}(\text{NH}_3)_2^+(\text{aq})$, because $K_{eq3} = 1.6 \times 10^7$

- D) $\text{Ag}(\text{NH}_3)_2^+(\text{aq})$, because $K_{eq1} < K_{eq2}$

a) A 55.8 g sample of $\text{AsF}_5(\text{g})$ is introduced into an evacuated 10.5 L container at 105°C .

i) What is the initial molar concentration of $\text{AsF}_5(\text{g})$ in the container? (2pts)

$$55.8 \text{ g AsF}_5 \left| \frac{1 \text{ mol AsF}_5}{169.92 \text{ g AsF}_5} \right. = \frac{0.328 \text{ mol}}{10.5 \text{ L}} = \boxed{0.0313 \text{ M AsF}_5}$$

ii) What is the initial pressure, in atmospheres, of the $\text{AsF}_5(\text{g})$ in the container? (2pts)

$$PV = nRT$$

$$(P)(10.5 \text{ L}) = (0.328 \text{ mol}) \left(0.08206 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \right) (378 \text{ K})$$

$$\boxed{P = 0.969 \text{ atm}}$$

At 105°C , $\text{AsF}_5(\text{g})$ decomposes into $\text{AsF}_3(\text{g})$ and $\text{F}_2(\text{g})$ according to the following chemical equation.



b) In terms of molar concentrations, write the equilibrium-constant expression for the decomposition of $\text{AsF}_5(\text{g})$.

$$K_{eq} = \frac{[\text{AsF}_3][\text{F}_2]}{[\text{AsF}_5]}$$

c) When equilibrium is established, 27.7 percent of the original number of moles of $\text{AsF}_5(\text{g})$ has decomposed.

i) Calculate the molar concentration of $\text{AsF}_5(\text{g})$ at equilibrium. (1pt)

$$0.328 \text{ mol} \cdot 0.723 = \frac{0.237 \text{ mol}}{10.5 \text{ L}} = \boxed{0.0226 \text{ M AsF}_5}$$

(9% left in container)

ii) Using molar concentrations, calculate the value of the equilibrium constant, K_{eq} , at 105°C . (3pts)

AsF_5	\rightleftharpoons	AsF_3	$+$	F_2	(1:1 ratio)
0.0313		0		0	
$\rightarrow 0.0087$		$+ 0.0087$		$+ 0.0087$	
0.0226		0.0087		0.0087	

$$K_{eq} = \frac{[0.0087]^2}{[0.0226]}$$

$$\boxed{K_{eq} = 0.033}$$

d) Calculate the mole fraction of $\text{F}_2(\text{g})$ in the container at equilibrium. (1pt)

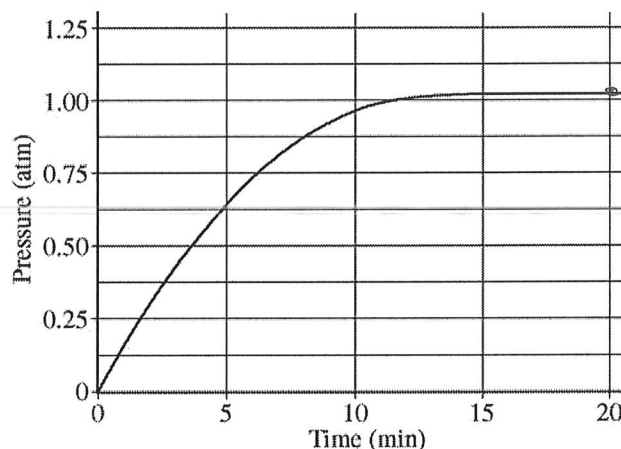
(can use M) (or convert to moles if you wish)

$$\frac{0.0087}{2(0.0087) + (0.0226)} = \boxed{0.217}$$



2014 4

- 2) When heated, calcium carbonate decomposes according to the equation above. In a study of the decomposition of calcium carbonate, a student added a 50.0 g sample of powdered $\text{CaCO}_3(s)$ to a 1.00 L rigid container. The student sealed the container, pumped out all the gases, then heated the container in an oven at 1100 K. As the container was heated, the total pressure of the $\text{CO}_2(g)$ in the container was measured over time. The data are plotted in the graph.



The student repeated the experiment, but this time the student used a 100.0 g sample of powdered $\text{CaCO}_3(s)$. In this experiment, the final pressure in the container was 1.04 atm, which was the same final pressure as in the first experiment.

- a) Calculate the number of moles of $\text{CO}_2(g)$ present in the container after 20 minutes of heating. (2pts)

$$PV = nRT$$

$$(1.04 \text{ atm})(1.00 \text{ L}) = (n) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (1100 \text{ K})$$

$$n = 0.012 \text{ mol CO}_2$$

- b) The student claimed that the final pressure in the container in each experiment became constant because all of the $\text{CaCO}_3(s)$ had decomposed. Based on the data in the experiments, do you agree with this claim? Explain. (2pts)

No, the reaction reached equilibrium and the pressure (caused by CO_2) became constant.

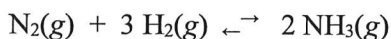
- c) After 20 minutes some $\text{CO}_2(g)$ was injected into the container, initially raising the pressure to 1.5 atm. Would the final pressure inside the container be less than, greater than, or equal to 1.04 atm? Explain your reasoning. (2pts)

Equal to 1.04. The initial P would increase and the reaction would shift left until it returns to 1.04. (CO_2 is the only gas in the system)

- d) Are there sufficient data obtained in the experiments to determine the value of the equilibrium constant, K_p , for the decomposition of $\text{CaCO}_3(s)$ at 1100 K? Justify your answer. (1pt)

Yes $K_p = P_{\text{CO}_2}$ no solids in the expression

$$P_{\text{CO}_2} = 1.04 \text{ atm}, \text{ so } K = 1.04.$$



2004B 1

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. (2pts)

$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3}$$

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

$$P_{\text{N}_2} = 0.411 \text{ atm}, P_{\text{H}_2} = 0.903 \text{ atm}, \text{ and } P_{\text{NH}_3} = 0.224 \text{ atm}.$$

i) Calculate the value of the reaction quotient, Q , at these initial conditions. (1pt)

$$Q = \frac{(0.224)^2}{(0.411)(0.903)^3} = \boxed{0.166}$$

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. (2pts)

$Q > K$, rxn will shift left to establish equilibrium.

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} .

$$K_p = K_c(RT)^{\Delta n} \quad \Delta n = 2 - 4 = -2$$

$$K_p = K_c(RT)^{-2} \quad \text{This calc is no longer required in 2004 was more fun}$$

$$K_p = \frac{K_c}{(RT)^2} \quad K_c = K_p(RT)^2$$

$$K_c = (3.1 \times 10^{-4})(0.08206 \cdot 700)^2 = \boxed{1.0}$$

d) The value of K_p for the reaction represented here is 8.3×10^{-3} at 700. K. $\text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g}) \rightleftharpoons \text{NH}_4\text{HS}(\text{g})$

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

i) $\text{NH}_4\text{HS}(\text{g}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$ (1pt) reverse rxn

$$K_p = \frac{1}{8.3 \times 10^{-3}} = \boxed{120}$$

ii) $2 \text{H}_2\text{S}(\text{g}) + \text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_4\text{HS}(\text{g})$ (2pts) (Added to rxn at top of page)



$$K_p = (8.3 \times 10^{-3})^2$$

$$K_p = 3.1 \times 10^{-4}$$

$$K_p = (8.3 \times 10^{-3})^2 (3.1 \times 10^{-4}) = \boxed{2.1 \times 10^{-8}}$$



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. (1pt each)

- a) The effect on the equilibrium partial pressure of NH_3 gas when additional solid NH_4HS is introduced into the container.

No effect. A solid is not a part of the equilibrium expression

- b) The effect on the equilibrium partial pressure of NH_3 gas when additional H_2S gas is introduced into the container.

P_{NH_3} will decrease. The rxn will shift to the left and consume NH_3 as it does.

- c) The effect on the mass of solid NH_4HS present when the volume of the container is decreased.

$V \downarrow$, so $P \uparrow$. The reaction will shift to the left to reduce the stress of the extra pressure. This will cause an increase in mass of NH_4HS .

- d) The effect on the mass of solid NH_4HS present when the temperature is increased.

The mass will decrease. The reaction will shift to the right because it's endothermic. This will cause more of the NH_4HS to decompose.

Ammonium hydrogen sulfide is a crystalline solid that decomposes: $\text{NH}_4\text{HS}(s) \leftrightarrow \text{NH}_3(g) + \text{H}_2\text{S}(g)$ 1981

- 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 value at 25°C .

$$P_{\text{total}} = P_{\text{NH}_3} + P_{\text{H}_2\text{S}}$$

$$K_P = (P_{\text{NH}_3})(P_{\text{H}_2\text{S}})$$

$$P \text{ of each gas} = 0.330 \text{ atm}$$

$$= (0.330)^2 = \boxed{0.109}$$

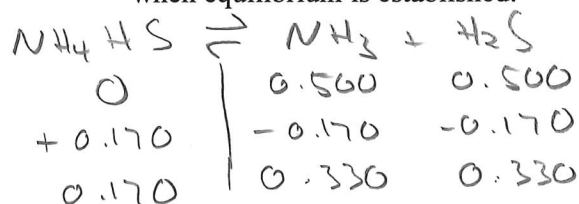
- b) Some extra NH_3 gas is injected into the vessel containing the sample described in part (a). When equilibrium is reestablished at 25°C , the partial pressure of NH_3 in the vessel is twice the partial pressure of H_2S . Calculate the numerical value of the partial pressure of NH_3 and the partial pressure of H_2S in the vessel after the NH_3 has been added and the equilibrium has been reestablished.

$$K_P = (2x)(x) \rightarrow x = 0.233$$

$$0.109 = 2x^2$$

$$P_{\text{NH}_3} = 2(0.233) = \boxed{0.466 \text{ atm}}$$

- 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 atmospheres. Calculate the number of moles of solid NH_4HS that is present when equilibrium is established.



Same Temp, so same K_P
 @ Equil.

$$PV = nRT$$

$$(0.170)(1.00) = (n)(0.08206)(298)$$

$$n = \boxed{0.00695 \text{ mol } \text{NH}_4\text{HS}}$$

1:1 ratio, so
 mole of either gas
 equals moles of $\text{NH}_4\text{HS}(s)$