1988 D

$$NH_4HS(s) \leftrightarrow NH_3(g) + H_2S(g)$$
  $\Delta H^0 = +93$  kilojoules

The equilibrium above is established by placing solid NH<sub>4</sub>HS in an evacuated container at 25°C. At equilibrium, some solid NH<sub>4</sub>HS remains in the container. Predict and explain each of the following.

- (a) The effect on the equilibrium partial pressure of NH<sub>3</sub> gas when additional solid NH<sub>4</sub>HS is introduced into the container
- (b) The effect on the equilibrium partial pressure of NH<sub>3</sub> gas when additional H<sub>2</sub>S is introduced into the container
- (c) The effect on the mass of solid NH<sub>4</sub>HS present when the volume of the container is decreased
- (d) The effect on the mass of solid NH<sub>4</sub>HS present when the temperature is increased.

1992 A

$$2 \text{ NaHCO}_3(s) \Leftrightarrow \text{Na}_2\text{CO}_3(s) + \text{H}_2\text{O}(g) + \text{CO}_2(g)$$

Solid sodium hydrogen carbonate, NaHCO<sub>3</sub>, decomposes on heating according to the equation above.

- (a) A sample of 100. grams of solid NaHCO<sub>3</sub> 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<sub>2</sub>O<sub>(g)</sub> present at equilibrium.
- (b) How many grams of the original solid remain in the container under the conditions described in (a)?
- (c) Write the equilibrium expression for the equilibrium constant,  $K_P$ , and calculate its value for the reaction under the conditions in (a).
- (d) If 110. grams of solid NaHCO<sub>3</sub> had been placed in the 5.00-liter container and heated to 160°C, what would the total pressure have been at equilibrium? Explain.

1994 A

$$MgF_{2}(s) \Leftrightarrow Mg^{2+}(aq) + 2 F^{-}(aq)$$

In a saturated solution of MgF<sub>2</sub> at 18°C, the concentration of Mg<sup>2+</sup> is  $1.21 \times 10^{-3}$  molar. The equilibrium is represented by the equation above.

- (a) Write the expression for the solubility-product constant,  $K_{sp}$ , and calculate its value at 18°C.
- (b) Calculate the equilibrium concentration of Mg<sup>2+</sup> in 1.000 liter of saturated MgF<sub>2</sub> solution at 18°C to which 0.100 mole of solid KF has been added. The KF dissolves completely. Assume the volume change is negligible.
- (c) Predict whether a precipitate of MgF<sub>2</sub> will form when 100.0 milliliters of a 3.00×10<sup>-3</sup>-molar Mg(NO<sub>3</sub>)<sub>2</sub> solution is mixed with 200.0 milliliters of a 2.00×10<sup>-3</sup>-molar NaF solution at 18°C. Calculations to support your prediction must be shown.
- (d) At 27°C the concentration of  $Mg^{2+}$  in a saturated solution of  $MgF_2$  is  $1.17 \times 10^{-3}$  molar. Is the dissolving of  $MgF_2$  in water an endothermic or an exothermic process? Give an explanation to support your conclusion.

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

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.

$$[H_2] = 0.20 \text{ mol/L} \\ [CO_2] = 0.30 \text{ mol/L} \\ [H_2O] = [CO] = 0.55 \text{ mol/L}$$

- (a) What is the mole fraction of CO(g) in the equilibrium mixture?
- (b) Using the equilibrium concentrations given above, calculate the value of  $K_c$ , the equilibrium constant for the reaction.
- (c) Determine  $K_p$  in terms of  $K_c$  for this system.
- (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.
- (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.

1998 D

$$C(s) + H_2O(g) \Leftrightarrow CO(g) + H_2(g)$$
  $\Delta H^o = +131kJ$ 

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. 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.
- (b) The temperature of the equilibrium mixture is increased at constant volume.
- (c) The volume of the container is decreased at constant temperature.
- (d) The graphite pellets are pulverized.

2000 A

$$2 \text{ H}_2\text{S}(g) \rightarrow 2 \text{ H}_2(g) + \text{S}_2(g)$$

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  $3.72 \times 10^{-2}$  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.
- (b) Calculate the equilibrium concentration, in mol·L<sup>-1</sup>, of the following gases in the container at 483 K.
  - (i)  $H_2(g)$
  - (ii)  $H_2S(g)$
- (c) Calculate the value of the equilibrium constant,  $K_c$ , for the decomposition reaction at 483 K.
- (d) Calculate the partial pressure of  $S_{2(g)}$  in the container at equilibrium at 483 K.
- (e) For the reaction  $H_{2(g)} + \frac{1}{2} S_{2(g)} \rightarrow H_2S_{(g)}$  at 483 K, calculate the value of the equilibrium constant,  $K_c$ .

### 1988 D Answer:

- (a) The equilibrium pressure of NH<sub>3</sub> gas would be unaffected.  $K_P = (P_{NH3})(P_{H2S})$ . Thus the amount of solid NH<sub>4</sub>HS present does not affect the equilibrium.
- (b) The equilibrium pressure of NH<sub>3</sub> gas would decrease. In order for the pressure equilibrium constant, K<sub>P</sub>, to remain constant, the equilibrium pressure of NH<sub>3</sub> must decrease when the pressure of H<sub>2</sub>S is increased.  $K_P =$  $(P_{NH3})(P_{H2S})$ . (A complete explanation based on LeChatelier's principle is also acceptable.)
- (c) The mass of NH<sub>4</sub>HS 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. The decrease is realized by the formation of more solid NH<sub>4</sub>HS.  $K_p = (P_{NH3})(P_{H2S})$ . (A complete explanation based on LeChatelier's principle is also acceptable.)
- (d) The mass of NH<sub>4</sub>HS decreases because the endothermic reaction absorbs heat and goes nearer to completion (to the right) as the temperature increases.

# 1992 A Answer:

(a) 
$$n_{gas} = \frac{PV}{RT} = \frac{(7.76atm)(5.00L)}{(0.0821\frac{L_atm}{mol \ K})(433K)} = 1.09mol$$

$$\begin{array}{l} mol\ H_2O = (^{1}\!/_{2})(1.09\ mol) = 0.545\ mol\ H_2O(g) \\ (b)\ 0.545mol\ H_2O \times \frac{2mol\ NaHCO_{3}}{1mol\ H_2O} \times \frac{84.0gNaHCO_{3}}{1\ mol} = 91.9\ g\ NaHCO_{3}\ decomposed \end{array}$$

remaining = 100.g - 91.6g = 8.4g

OR

100 - 
$$\left(0.545 \text{ mol H}_2\text{O} \times \frac{18.0 \text{ g}}{1 \text{ mol}} + 0.545 \text{ mol CO}_2 \times \frac{44.0 \text{ g}}{1 \text{ mol}}\right)$$

= 100g - 33.8g = 66g (or 66.2g) [includes Na<sub>2</sub>CO<sub>3</sub> solid in this mass]

- (c)  $K_p = (P_{H2O})(P_{CO2}) = (3.88)(3.88) \text{atm}^2 = 15.1 \text{ atm}^2$
- (d) Pressure would remain at 7.76 atm. Since some solid remained when 100.g was used (and there has been no temperature change), then using 110g will not affect the equilibrium.

### 1994 A Answer:

(a) 
$$K_{sp} = [Mg^{2+}][F^{-}]^2 = (1.21 \times 10^{-3})(2.42 \times 10^{-3})^2$$
  
= 7.09×10<sup>-9</sup>

(b)  $X = \text{concentration loss by Mg}^{2+} \text{ ion }$ 

 $2X = \text{concentration loss by } F^{-} \text{ ion }$ 

$$[Mg^{2+}] = (1.21 \times 10^{-3} - X) M$$

$$[F^{-}] = (0.100 + 2.42 \times 10^{-3} - 2X) M$$

since X is a small number then  $(0.100 + 2.42 \times 10^{-3} - 2X) \approx 0.100$ 

$$K_{sp} = 7.09 \times 10^{-9} = (1.21 \times 10^{-3} - X)(0.100)^2$$

 $X = 1.2092914 \times 10^{-3}$ 

$$[Mg^{2^+}] = 1.21 \times 10^{-3} - 1.20929 \times 10^{-3} = 7.09 \times 10^{-7}M$$

## 1994 A Answer (continued):

- (c)  $[Mg^{2+}] = 3.00 \times 10^{-3} M \times 100.0 \text{ mL}/300.0 \text{ mL} = 1.00 \times 10^{-3} M$   $[F^{-}] = 2.00 \times 10^{-3} M \times 200.0 \text{ mL}/300.0 \text{ mL} = 1.33 \times 10^{-3} M$   $\text{trial } K_{sp} = (1.00 \times 10^{-3})(1.33 \times 10^{-3})^2 = 1.78 \times 10^{-9}$  $\text{trial } K_{sp} < = 7.09 \times 10^{-9}, \therefore \text{ no ppt.}$
- (d) @ 18°C,  $1.21 \times 10^{-3}$  M MgF<sub>2</sub> dissolves @ 27°C,  $1.17 \times 10^{-3}$  M MgF<sub>2</sub> dissolves MgF<sub>2</sub>  $\Leftrightarrow$  Mg<sup>2+</sup> + 2 F<sup>-</sup> + heat

dissolving is exothermic; if heat is increased it forces the equilibrium to shift left (according to LeChatelier's Principle) and less MgF<sub>2</sub> will dissolve.

## 1995 A Answer:

- (a) CO = f(0.55 mol, 1.6 mol) = 0.34
- (b)  $K_c = ([H_2O][CO])/([H_2][CO_2]) = (0.55 \times 0.55)/(0.20 \times 0.30) = 5.04$
- (c) since  $\Delta n = 0$ ,  $K_c = K_p$
- (d) [CO] = 0.55 30.0% = 0.55 0.165 = 0.385 M [H<sub>2</sub>O] = 0.55 - 0.165 = 0.385 M [H<sub>2</sub>] = 0.20 + 0.165 = 0.365 M [CO<sub>2</sub>] = 0.30 + 0.165 = 0.465 M K =  $(0.385)^2/(0.365 \times 0.465) = 0.87$
- (e) let  $X = \Delta[H_2]$  to reach equilibrium  $[H_2] = 0.50 \text{ mol/} 3.0 \text{L} - X = 0.167 - X$   $[CO_2] = 0.50 \text{ mol/} 3.0 \text{L} - X = 0.167 - X$  [CO] = +X;  $[H_2O] = +X$  $K = X^2/(0.167 - X)^2 = 5.04$ ; X = [CO] = 0.12 M

### 1998 D Answer:

- (a) CO will decrease. An increase of hydrogen gas molecule will increase the rate of the reverse reaction which consumes CO. A LeChatelier Principle shift to the left.
- (b) CO will increase. Since the forward reaction is endothermic (a  $\Delta H > 0$ ) an increase in temperature will cause the forward reaction to increase its rate and produce more CO. A LeChatelier Principle shift to the right.
- (c) CO will decrease. A decrease in volume will result in an increase in pressure, the equilibrium will shift to the side with fewer gas molecules to decrease the pressure, ∴, a shift to the left.
- (d) CO will remain the same. Once at equilibrium, the size of the solid will affect neither the reaction rates nor the equilibrium nor the concentrations of reactants or products.

2000 A Answer:

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

(b) (i) 
$$\frac{3.72 \times 10^{-2} \text{ mol } S_2}{1.25 \text{ L}} \times \frac{2 \text{ mol } H_2}{1 \text{ mol } S_2} = 5.95 \times 10^{-2} M H_2$$

(ii) 
$$\frac{\left(3.40 \text{ g H}_{2}\text{S}? \frac{1 \text{ mol}}{34.0 \text{ g}}\right) - \left(3.72? 10^{2} \text{mol S}_{2}? \frac{2 \text{ mol H}_{2}\text{S}}{1 \text{ mol S}_{2}}\right)}{1.25 \text{ L}} = 2.05 \times 10^{-2} M \text{ H}_{2}\text{S}$$
(c) 
$$K_{c} = \frac{\left[5.952 \times 10^{-2}\right]^{2} \left[\frac{3.72 \times 10^{-2}}{1.25}\right]}{\left[0.02048\right]^{2}} = 0.251$$

(c) 
$$K_c = \frac{\left[5.952 \times 10^{-2}\right]^2 \left[\frac{3.72 \times 10^{-2}}{1.25}\right]}{\left[0.02048\right]^2} = 0.251$$

(d) 
$$PV=nRT = 1.18$$

(e) 
$$K'_c = \sqrt{\frac{1}{K_c}} = 2.00$$