



Solid sodium hydrogen carbonate,  $\text{NaHCO}_3$ , decomposes on heating according to the equation above.

(a) A sample of 100. grams of solid  $\text{NaHCO}_3$  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  $\text{H}_2\text{O}(\text{g})$  present at equilibrium.

(b) How many grams of the original solid remained 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  $\text{NaHCO}_3$  had been placed in the 5.00-liter container and heated to 160 °C, what would the total pressure have been at equilibrium? Explain.

ANSWER:

1) average points = 3.9

a) three points

mole fraction is 50:50 from equation

therefore  $7.76 \text{ atm} \div 2 = 3.88 \text{ atm}$  (contribution by  $\text{H}_2\text{O}$ )

$PV = nRT$ ; rearrange to get  $n = (PV) \div (RT)$

$n = [(3.88 \text{ atm})(5.00 \text{ L})] \div [(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(433 \text{ K})]$

$= 0.545 \text{ mol}$

Personal note by John Park: the actual AP standard uses 7.76 atm in its  $PV = nRT$  calculation and then applies the 50:50 criterion to the value for  $n$  (1.09 mol) calculated. I prefer the above explanation.

b) two points

from equation, the ratio of  $\text{NaHCO}_3$  to  $\text{H}_2\text{O}$  is 2:1

$x / 0.545 = 2 / 1$

$x = 1.09 \text{ mol}$  of  $\text{NaHCO}_3$  decomposed

$1.09 \text{ mole} \times 84.01 \text{ g/mol} = 91.6 \text{ g}$  of  $\text{NaHCO}_3$  decomposed

$100. \text{ g} - 91.6 \text{ g} = 8.4 \text{ g}$  of  $\text{NaHCO}_3$  remaining

c) two points

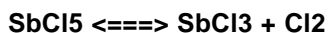
$K_p = (P_{\text{H}_2\text{O}})(P_{\text{CO}_2})$

$= (3.88 \text{ atm})(3.88 \text{ atm}) = 15.1 \text{ atm}^2$

d) two points

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.

2. At elevated temperatures,  $\text{SbCl}_5$  gas decomposes into  $\text{SbCl}_3$  gas and  $\text{Cl}_2$  gas, as shown by the following equation.



a) An 89.7-gram sample of  $\text{SbCl}_5$  (molecular weight 299.0) is placed in an evacuated 15.0-liter container at 182 °C.

(1) What is the concentration in moles per liter of  $\text{SbCl}_5$  in the container before any decomposition occurs?

(2) What is the pressure in atmospheres of  $\text{SbCl}_5$  in the container before any decomposition occurs?

b) If the  $\text{SbCl}_5$  is 29.2 percent decomposes 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  $K_c$ .

c) In order to produce some  $\text{SbCl}_5$ , a 1.00-mole sample of  $\text{SbCl}_3$  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  $\text{Cl}_2$  must be added to this container to reduce the number of moles of  $\text{SbCl}_3$  to 0.700 mole at equilibrium?

ANSWER:

a) four points

$$(1) 89.7 \text{ g SbCl}_5 / 299.0 \text{ g mole} = 0.300 \text{ mole SbCl}_5$$

$$[\text{SbCl}_5] \text{ initial} = 0.300 \text{ mole} / 15.0 \text{ liter} = 0.200 \text{ M}$$

$$(2) T = 182 \text{ }^\circ\text{C} + 273 = 455 \text{ K}$$

$$P = nRT / V = [(0.300 \text{ mole}) (0.0821 \text{ L atm}) (455 \text{ K})] / [(15.0 \text{ L}) (\text{mole K})] = 0.747 \text{ atm}$$

OR

$$(15.0 \text{ L} / 0.300 \text{ mol}) \times (273 \text{ K} / 455 \text{ K}) = 30.0 \text{ L} / \text{mol} \text{ (at std. temperature)}$$

$$1 \text{ atm} \times [(22.4 \text{ L} / \text{mol}) \div (30.0 \text{ L} / \text{mol})] = 0.747 \text{ atm}$$

b) three points

Equilibrium concentrations:

$$[\text{SbCl}_3] = [\text{Cl}_2] = (0.0200 \text{ mol} / \text{L}) \times 0.292 = 5.84 \times 10^{-3} \text{ M}$$

$$[\text{SbCl}_5] = (0.0200 \text{ mol L}) \times 0.708 \text{ L} = 1.42 \times 10^{-2} \text{ M}$$

$$K_c = ([\text{SbCl}_3][\text{Cl}_2]) \div [\text{SbCl}_5] = (5.84 \times 10^{-3})^2 \div (1.42 \times 10^{-2}) = 2.41 \times 10^{-3}$$

OR

Equilibrium pressures:

$$P_{\text{SbCl}_3} = P_{\text{Cl}_2}$$

$$= 0.747 \text{ atm} \times 0.292 = 0.218 \text{ atm}$$

$$P_{\text{SbCl}_5} = 0.747 \text{ atm} \times 0.708 = 0.529 \text{ atm}$$

$$K_p = (P_{\text{SbCl}_3} \times P_{\text{Cl}_2}) \div P_{\text{SbCl}_5} = (0.218)^2 \div 0.529 = 8.98 \times 10^{-2}$$

c) two points

$$K = ([\text{SbCl}_3][\text{Cl}_2]) \div [\text{SbCl}_5] = 0.117$$

Equilibrium concentrations:

$$[\text{SbCl}_5] = (1.00 - 0.70) \text{ mol} / 2.00 \text{ L} = 0.15 \text{ M}$$

$$[\text{SbCl}_3] = 0.700 \text{ mole} / 2.00 \text{ L} = 0.350 \text{ M}$$

$$[\text{Cl}_2] = x$$

$$K_c = [(0.350)(x)] \div (0.15) = 0.117$$

$$x = [\text{Cl}_2] = 0.50 \text{ M}$$

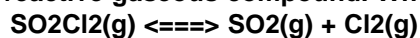
$$\text{Moles Cl}_2 \text{ at equilibrium} = 0.050 \text{ mol L} \times 2.00 \text{ L} = 0.10 \text{ mol}$$

$$\text{Moles Cl}_2 \text{ needed to make } 0.300 \text{ mol SbCl}_3 \text{ into SbCl}_5 = 0.30 \text{ mol}$$

$$\text{Moles Cl}_2 \text{ that must be added} = 0.40 \text{ mol}$$

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**3. Sulfuryl chloride, SO<sub>2</sub>Cl<sub>2</sub>, is a highly reactive gaseous compound. When heated, it decomposes as follows.**



**This decomposition is endothermic. A sample of 3.509 grams of SO<sub>2</sub>Cl<sub>2</sub> 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<sub>2</sub>Cl<sub>2</sub>(g) occurred?**

**(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<sub>2</sub>, Cl<sub>2</sub>, and SO<sub>2</sub>Cl<sub>2</sub> at equilibrium at 375 K.**

**(c) Give the expression for the equilibrium constant (either K<sub>p</sub> or K<sub>c</sub>) for the decomposition of SO<sub>2</sub>Cl<sub>2</sub>(g) at 375 K. Calculate the value of the equilibrium constant you have given, and specify its units.**

**(d) If the temperature were raised to 500 K, what effect would this have on the equilibrium constant? Explain briefly.**

ANSWER:

a) two points

$$n = 3.509 \text{ g} \div 135.0 \text{ g/mol}$$

$$P = (nRT) / V$$

$$= [(0.02600 \text{ mol}) (0.08205 \text{ L atm mol}^{-1} \text{ K}^{-1}) (375 \text{ K})] / 1.00 \text{ L}$$

$$P = 0.800 \text{ atm}$$

b) three points

$$P_{\text{SO}_2\text{Cl}_2} = 0.800 \text{ atm} - y \text{ atm}$$

$$\begin{aligned}
 P_{\text{SO}_2} &= P_{\text{Cl}_2} = y \text{ atm} \\
 P_{\text{tot}} &= P_{\text{SO}_2\text{Cl}_2} + P_{\text{SO}_2} + P_{\text{Cl}_2} \\
 1.43 \text{ atm} &= 0.800 \text{ atm} - y + y + y \text{ (by substitution)} \\
 P_{\text{SO}_2} &= P_{\text{Cl}_2} = y = 0.63 \text{ atm} \\
 P_{\text{SO}_2\text{Cl}_2} &= 0.800 - 0.63 = 0.17 \text{ atm}
 \end{aligned}$$

c) three points

$$K_p = (P_{\text{SO}_2} \times P_{\text{Cl}_2}) / P_{\text{SO}_2\text{Cl}_2}$$

$$K_p = (0.63 \text{ atm})^2 / 0.17 \text{ atm}$$

$$K_p = 2.3 \text{ atm}$$

Alternative approach in (b) and (c) is to determine the number of moles of each species, then molarity, and finally  $K_c$ .

$$n_{\text{SO}_2\text{Cl}_2} = 0.0260 - z$$

$$n_{\text{SO}_2} = n_{\text{Cl}_2} = z \text{ mol}$$

$$n_{\text{tot}} = n_{\text{SO}_2\text{Cl}_2} + n_{\text{SO}_2} + n_{\text{Cl}_2}$$

$$n_{\text{tot}} = PV / RT = (1.43 \text{ atm} \times 1.00 \text{ L}) / (0.08205 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 375 \text{ K})$$

$$n_{\text{tot}} = 0.0465 \text{ mol} = 0.0260 - z + z + z$$

$$n_{\text{Cl}_2} = n_{\text{SO}_2} = z = 0.0205 \text{ mol}$$

$$n_{\text{SO}_2\text{Cl}_2} = 0.0260 - 0.0205 = 0.00550 \text{ mol}$$

$$K_c = ([\text{SO}_2][\text{Cl}_2]) / [\text{SO}_2\text{Cl}_2]$$

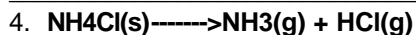
$$K_c = [0.0205]^2 / [0.0055]$$

$$K_c = 0.076 \text{ M}$$

d) one point

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.

A maximum of 1 point was deducted for math for unit errors or for reporting an unreasonable number of significant figures. This same procedure was also used for Problems 2 and 3.



for this reaction,  $\Delta H = +42.1$  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  $\text{NH}_3\text{(g)}$  will have increased, decreased, or remained the same when equilibrium is reestablished after each of the following disturbances of the original system. Some solid  $\text{NH}_4\text{Cl}$  remains in the flask at all times. Justify each answer with a one- or two-sentence explanation.

- A small quantity of  $\text{NH}_4\text{Cl}$  is added.
- The temperature of the system is increased.
- the volume of the system is increased.
- A quantity of gaseous  $\text{HCl}$  is added.
- A quantity of gaseous  $\text{NH}_3$  is added.

ANSWER:

5 effects and 5 explanations, valued at 0.8 point each. Proper prediction of equilibrium shift was necessary in order to receive credit for an explanation.

$P_{\text{NH}_3}$  Explanation

- same Solid has constant concentration (activity is unity): therefore, no equilibrium shift.
- increased Reaction shifts in favor of gases because reaction is endothermic.
- same As volume increases, reaction is driven to the right, producing  $\text{NH}_3$  and  $\text{HCl}$  so as to yield same partial pressure of each gas at the new equilibrium.
- decreased Reaction shifts left to relieve stress of added  $\text{HCl}$ , consuming  $\text{NH}_3$  and reducing its partial pressure.
- increased Added  $\text{NH}_3$  causes equilibrium shift in favor of solid  $\text{NH}_4\text{Cl}$ ; however, only part of the added  $\text{NH}_3$  reacts so that  $P_{\text{NH}_3}$  will be greater than the original.