# The Advanced Placement Examination in Chemistry 

## Part II - Free Response Questions \& Answers 1970 to 2006

## Electrochemistry

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## 1977 D

For the system $2 \mathrm{SO}_{2(g)}+\mathrm{O}_{2}(g) \leftrightarrow 2 \mathrm{SO}_{3}(g), \Delta H$ is negative for the production of $\mathrm{SO}_{3}$. Assume that one has an equilibrium mixture of these substances. Predict the effect of each of the following changes on the value of the equilibrium constant and on the number of moles of $\mathrm{SO}_{3}$ present in the mixture at equilibrium. Briefly account for each of your predictions. (Assume that in each case all other factors remain constant.)
(a) Decreasing the volume of the system.
(b) Adding oxygen to the equilibrium mixture.
(c) Raising the temperature of the system.

Answer:
(a) As volume decreases, pressure increases and the reaction shifts in the direction of fewer molecules (less volume; more $\mathrm{SO}_{3}$ ) to relieve the stress. Value of $\mathrm{K}_{\text {eq }}$ does not change.
(b) Additional $\mathrm{O}_{2}$ disturbs the equilibrium and $\mathrm{SO}_{3}$ is formed to relieve the stress. Value of $\mathrm{K}_{\mathrm{eq}}$ does not change.
(c) Increase in temperature shifts the reaction to the left to "use up" some of the added heat. Less $\mathrm{SO}_{3}$ remains. Value of $\mathrm{K}_{\mathrm{eq}}$ decreases due to the relative greater increase in the rate of the endothermic reaction (reaction to the left).

1980 D
$\mathrm{NH}_{4} \mathrm{Cl}(s) \leftrightarrow \mathrm{NH}_{3}(g)+\mathrm{HCl}_{(g)} \quad \Delta H=+42.1$ 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 $\mathrm{NH}_{3}(\mathrm{~g})$ will have increased, decreased, or remained the same when equilibrium is reestablished after each of the following disturbances of the original system. Some solid $\mathrm{NH}_{4} \mathrm{Cl}$ remains in the flask at all times. Justify each answer with a one-or-two sentence explanation.
(a) A small quantity of $\mathrm{NH}_{4} \mathrm{Cl}$ is added.
(b) The temperature of the system is increased.
(c) The volume of the system is increased.
(d) A quantity of gaseous HCl is added.
(e) A quantity of gaseous $\mathrm{NH}_{3}$ is added.

Answer:
(a) $\mathrm{P}_{\mathrm{NH}}$ does not change. Since $\mathrm{NH}_{4} \mathrm{Cl}_{(s)}$ has constant concentration ( $\mathrm{a}=1$ ), equilibrium does not shift.
(b) $\mathrm{P}_{\mathrm{NH} 3}$ increases. Since the reaction is endothermic, increasing the temperature shifts the equilibrium to the right and more $\mathrm{NH}_{3}$ is present.
(c) $\mathrm{P}_{\mathrm{NH}}$ does not change. As V increases, some solid $\mathrm{NH}_{4} \mathrm{Cl}$ decomposes to produce more $\mathrm{NH}_{3}$. But as the volume increases, $\mathrm{P}_{\mathrm{NH} 3}$ remains constant due to the additional decomposition.
(d) $\mathrm{P}_{\mathrm{NH}}$ decreases. Some $\mathrm{NH}_{3}$ reacts with the added HCl to relieve the stress from the HCl addition.
(e) $\mathrm{P}_{\mathrm{NH}}$ increases. Some of the added $\mathrm{NH}_{3}$ reacts with HCl to relieve the stress, but only a part of the added $\mathrm{NH}_{3}$ reacts, so $\mathrm{P}_{\mathrm{NH} 3}$ increases.

1981 A
Ammonium hydrogen sulfide is a crystalline solid that decomposes as follows:

$$
\mathrm{NH}_{4} \mathrm{HS}(s) \leftrightarrow \mathrm{NH}_{3}(g)+\mathrm{H}_{2} \mathrm{~S}(g)
$$

(a) Some solid $\mathrm{NH}_{4} \mathrm{HS}$ is placed in an evacuated vessel at $25^{\circ} \mathrm{C}$. After equilibrium is attained, the total pressure inside the vessel is found to be 0.659 atmosphere. Some solid $\mathrm{NH}_{4} \mathrm{HS}$ remains in the vessel at equilibrium. For this decomposition, write the expression for $K_{P}$ and calculate its numerical value at $25^{\circ} \mathrm{C}$.

## Equilibrium

(b) Some extra $\mathrm{NH}_{3}$ gas is injected into the vessel containing the sample described in part (a). When equilibrium is reestablished at $25^{\circ} \mathrm{C}$, the partial pressure of $\mathrm{NH}_{3}$ in the vessel is twice the partial pressure of $\mathrm{H}_{2} \mathrm{~S}$. Calculate the numerical value of the partial pressure of $\mathrm{NH}_{3}$ and the partial pressure of $\mathrm{H}_{2} \mathrm{~S}$ in the vessel after the $\mathrm{NH}_{3}$ has been added and the equilibrium has been reestablished.
(c) In a different experiment, $\mathrm{NH}_{3}$ gas and $\mathrm{H}_{2} \mathrm{~S}$ gas are introduced into an empty 1.00 liter vessel at $25^{\circ} \mathrm{C}$. The initial partial pressure of each gas is 0.500 atmospheres. Calculate the number of moles of solid $\mathrm{NH}_{4} \mathrm{HS}$ that is present when equilibrium is established.
Answer:
(a) $\mathrm{K}_{\mathrm{P}}=\left(\mathrm{P}_{\mathrm{NH} 3}\right)\left(\mathrm{P}_{\mathrm{H} 2 \mathrm{~S}}\right)$
$\mathrm{P}_{\mathrm{NH} 3}=\mathrm{P}_{\mathrm{H} 2 \mathrm{~S}}=0.659 / 2 \mathrm{~atm}=0.330 \mathrm{~atm}$
$K_{P}=(0.330)^{2}=0.109$
(b) $\mathrm{P}_{\mathrm{NH} 3}=2 \mathrm{P}_{\mathrm{H} 2 \mathrm{~S}}$
$(2 x)(x)=0.109 ; x=0.233 \mathrm{~atm}=P_{\text {H2S }}$
$\mathrm{P}_{\mathrm{NH} 3}=0.466 \mathrm{~atm}$
(c) Equilibrium pressures of $\mathrm{NH}_{3}$ and $\mathrm{H}_{2} \mathrm{~S}$ are each 0.330 atm . Amounts of each $\mathrm{NH}_{3}$ and $\mathrm{H}_{2} \mathrm{~S}$ that have reacted correspond to $(0.500-0.330)=0.170 \mathrm{~atm}$.
$\mathrm{n}=\mathrm{mol}$ of each reactant $=\mathrm{mol}$ of solid product

$$
\mathrm{n}=\frac{\mathrm{PV}}{\mathrm{RT}}=\frac{(0.1 / 0 \mathrm{~atm})(1.00 \mathrm{~L})}{\left(0.08205 \frac{\mathrm{Latm}}{\mathrm{~mol} \mathrm{~K}}\right)(298 \mathrm{~K})}=6.95 \propto 10^{-3} \mathrm{~mol}
$$

1983 A
Sulfuryl chloride, $\mathrm{SO}_{2} \mathrm{Cl}_{2}$, is a highly reactive gaseous compound. When heated, it decomposes as follows: $\mathrm{SO}_{2} \mathrm{Cl}_{2(g)} \rightarrow \mathrm{SO}_{2(\mathrm{~g})}+\mathrm{Cl}_{2}(\mathrm{~g})$. This decomposition is endothermic. A sample of 3.509 grams of $\mathrm{SO}_{2} \mathrm{Cl}_{2}$ is placed in an evacuated 1.00 litre 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 $\mathrm{SO}_{2} \mathrm{Cl}_{2(g)}$ 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 $\mathrm{SO}_{2}, \mathrm{Cl}_{2}$, and $\mathrm{SO}_{2} \mathrm{Cl}_{2}$ at equilibrium at 375 K .
(c) Give the expression for the equilibrium constant (either $\mathrm{K}_{\mathrm{p}}$ or $\mathrm{K}_{\mathrm{c}}$ ) for the decomposition of $\mathrm{SO}_{2} \mathrm{Cl}_{2(g)}$ 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) $\mathrm{P}=\frac{\mathrm{n} R \mathrm{~T}}{\mathrm{~V}}=\frac{(3.509 \mathrm{~g})\left(\frac{1 \mathrm{~mol}}{135.0 \mathrm{~g}}\right)\left(0.0821 \frac{\mathrm{Lggtm}}{\mathrm{molgk}}\right)(375 \mathrm{~K})}{1.00 \mathrm{~L}}=0.800 \mathrm{~atm}$
(b) $\mathrm{P}_{\mathrm{SO} 2 \mathrm{Cl2}}=(0.800-\mathrm{y}) \mathrm{atm}$
$\mathrm{P}_{\mathrm{SO} 2}=\mathrm{P}_{\mathrm{Cl} 2}=\mathrm{y} \mathrm{atm}$
$\mathrm{P}_{\mathrm{T}}=\mathrm{P}_{\mathrm{SO} 2 \mathrm{Cl} 2}+\mathrm{P}_{\mathrm{SO} 2}+\mathrm{P}_{\mathrm{Cl} 2}$
$1.43 \mathrm{~atm}=(0.800-y+y+y)$ atm
$\mathrm{y}=0.63 \mathrm{~atm}=\mathrm{P}_{\mathrm{SO} 2}=\mathrm{P}_{\mathrm{C} 12}$
$\mathrm{P}_{\mathrm{SO} 2 \mathrm{C} 12}=(0.800-0.63) \mathrm{atm}=0.17 \mathrm{~atm}$
(c) $\mathrm{K}_{\mathrm{p}}=\frac{\left(\mathrm{P}_{\mathrm{SO}_{2}}\right)\left(\mathrm{P}_{\mathrm{Cl}_{2}}\right)}{\mathrm{P}_{\mathrm{SO}_{2} \mathrm{Cl}_{2}}}=\frac{(0.63 \mathrm{~atm})^{2}}{0.17 \mathrm{~atm}}=2.3 \mathrm{~atm}$

## Equilibrium

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(d) Heat is absorbed during the dissociation and so $\mathrm{K}_{500}>\mathrm{K}_{375}$. A stress is place on the system and K increases, which reduces the stress associated with the higher temperature.

1985 A
At $25^{\circ} \mathrm{C}$ the solubility product constant, $\mathrm{K}_{\mathrm{sp}}$, for strontium sulfate, $\mathrm{SrSO}_{4}$, is $7.6 \times 10^{-7}$. The solubility product constant for strontium fluoride, $\mathrm{SrF}_{2}$, is $7.9 \times 10^{-10}$.
(a) What is the molar solubility of $\mathrm{SrSO}_{4}$ in pure water at $25^{\circ} \mathrm{C}$ ?
(b) What is the molar solubility of $\mathrm{SrF}_{2}$ in pure water at $25^{\circ} \mathrm{C}$ ?
(c) An aqueous solution of $\mathrm{Sr}\left(\mathrm{NO}_{3}\right)_{2}$ is added slowly to 1.0 litre of a well-stirred solution containing 0.020 mole $\mathrm{F}^{-}$and 0.10 mole $\mathrm{SO}_{4}{ }^{2-}$ at $25^{\circ} \mathrm{C}$. (You may assume that the added $\mathrm{Sr}\left(\mathrm{NO}_{3}\right)_{2}$ solution does not materially affect the total volume of the system.)

1. Which salt precipitates first?
2. What is the concentration of strontium ion, $\mathrm{Sr}^{2+}$, in the solution when the first precipitate begins to form?
(d) As more $\operatorname{Sr}\left(\mathrm{NO}_{3}\right)_{2}$ is added to the mixture in (c) a second precipitate begins to form. At that stage, what percent of the anion of the first precipitate remains in solution?
Answer:
(a) $\mathrm{SrSO}_{4}(s) \leftrightarrow \mathrm{Sr}^{2+}(a q)+\mathrm{SO}_{4}{ }^{2-}(a q)$

At equilibrium: $\left[\mathrm{Sr}^{2+}\right]=X \mathrm{M}=\left[\mathrm{SO}_{4}{ }^{2-}\right]$
$X^{2}=\mathrm{K}_{\mathrm{sp}}=7.6 \times 10^{-7}$
$X=8.7 \times 10^{-4} \mathrm{~mol} / \mathrm{L}$, solubility of $\mathrm{SrSO}_{4}$
(b) $\mathrm{SrF}_{2}(s) \leftrightarrow \mathrm{Sr}^{2+}($ aq $)+2 \mathrm{~F}^{-}$(aq)

At equilibrium: $\left[\mathrm{Sr}^{2+}\right]=X \mathrm{M}=\left[\mathrm{F}^{-}\right]=2 X \mathrm{M}$
$\mathrm{K}_{\mathrm{SP}}=\left[\mathrm{Sr}^{2+}\right]\left[\mathrm{F}^{-}\right]^{2}=(X)(2 X)^{2}=7.9 \times 10^{-10}$
$X=5.8 \times 10^{-4} \mathrm{~mol} / \mathrm{L}$, solubility of $\mathrm{SrF}_{2}$
(c) Solve for $\left[\mathrm{Sr}^{2+}\right]$ required for precipitation of each salt.
$\mathrm{K}_{\text {sp }}=\left[\mathrm{Sr}^{2+}\right]\left[\mathrm{F}^{-}\right]^{2}=7.9 \times 10^{-10}=\mathrm{X} \times \frac{0.020 \mathrm{~mol}}{1 \mathrm{~mol}} ; \mathrm{X}=2.0 \times 10^{-6} \mathrm{M}$
$\mathrm{K}_{\text {sp }}=\left[\mathrm{Sr}^{2+}\right]\left[\mathrm{SO}_{4}{ }^{2-}\right]=7.6 \times 10^{-7}=\mathrm{Y} \times \frac{0.010 \mathrm{~mol}}{1.0 \mathrm{~L}} ; \mathrm{y}=7.6 \times 10^{-6} \mathrm{M}$
Since $2.0 \times 10^{-6} \mathrm{M}<7.6 \times 10^{-6} \mathrm{M}, \mathrm{SrF}_{2}$ must precipitate first.
When $\mathrm{SrF}_{2}$ precipitates, $\left[\mathrm{Sr}^{2+}\right]=2.0 \times 10^{-6} \mathrm{M}$
(d) The second precipitate to form is $\mathrm{SrSO}_{4}$, which appears when $\left[\mathrm{Sr}^{2+}\right]=7.6 \times 10^{-6} \mathrm{M}$ (based on calculations in Part c.)
When $\left[\mathrm{Sr}^{2+}\right]=7.6 \times 10^{-6} \mathrm{M},\left[\mathrm{F}^{-}\right]$is determined as follows:
$K_{\text {sp }}=\left[\mathrm{Sr}^{2+}\right]\left[\mathrm{F}^{-}\right]^{2}=7.9 \times 10^{-10}$
$=\left(7.6 \times 10^{-6}\right)(\mathrm{z})^{2}=7.9 \times 10^{-10} ; \mathrm{z}=1.0 \times 10^{-2} \mathrm{M}$
$\% \mathrm{~F}^{-}$still in solution $=\frac{1.0 \times 10^{-2}}{2.0 \times 10^{-2}} \times 100=50 . \%$

## Equilibrium

At elevated temperatures, $\mathrm{SbCl}_{5}$ gas decomposes into $\mathrm{SbCl}_{3}$ gas and $\mathrm{Cl}_{2}$ gas as shown by the following equation: $\mathrm{SbCl}_{5(\mathrm{~g})} \leftrightarrow \mathrm{SbCl}_{3}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g})$
(a) An 89.7 gram sample of $\mathrm{SbCl}_{5}$ (molecular weight 299.0 ) is placed in an evacuated 15.0 litre container at $182^{\circ} \mathrm{C}$.

1. What is the concentration in moles per litre of $\mathrm{SbCl}_{5}$ in the container before any decomposition occurs?
2. What is the pressure in atmospheres of $\mathrm{SbCl}_{5}$ in the container before any decomposition occurs?
(b) If the $\mathrm{SbCl}_{5}$ is 29.2 percent decomposed when equilibrium is established at $182^{\circ} \mathrm{C}$, calculate the value for either equilibrium constant $\mathrm{K}_{\mathrm{p}}$ or $\mathrm{K}_{\mathrm{c}}$, for this decomposition reaction. Indicated whether you are calculating $\mathrm{K}_{\mathrm{p}}$ or $\mathrm{K}_{\mathrm{c}}$.
(c) In order to produce some $\mathrm{SbCl}_{5}$, a 1.00 mole sample of $\mathrm{SbCl}_{3}$ is first placed in an empty 2.00 litre container maintained at a temperature different from $182^{\circ} \mathrm{C}$. At this temperature, $\mathrm{K}_{\mathrm{c}}$, equals 0.117 . How many moles of $\mathrm{Cl}_{2}$ must be added to this container to reduce the number of moles of $\mathrm{SbCl}_{3}$ to 0.700 mole at equilibrium?
Answer:
(a) (1)

$$
89.7 \mathrm{~g} \mathrm{SbCl}_{5} \times \frac{1 \mathrm{~mol}}{299.0 \mathrm{~g}}=0.300 \mathrm{~mol} \mathrm{SbCl}_{5}
$$

$$
\left[\mathrm{SbCl}_{5}\right]_{\text {init }}=\frac{0.300 \mathrm{~mol}}{15.0 \mathrm{~L}}=0.200 \mathrm{M}
$$

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

$$
\left.\left.\mathrm{P}=\frac{\mathrm{nRT}}{\mathrm{~V}}=\frac{(0.300 \mathrm{~mol})\left(0.0821 \frac{\mathrm{~L} \text { _atm }}{\mathrm{md} K} \mathrm{~K}\right.}{}\right)(455 \mathrm{~K}) \mathrm{L}\right)=0.747 \mathrm{~atm}
$$

## OR

$\frac{15.0 \mathrm{~L}}{0.300 \mathrm{~mol}} \times \frac{273 \mathrm{~K}}{455 \mathrm{~K}}=\frac{30.0 \mathrm{~L}}{\mathrm{~mol}}$ at std. temp.
$1 \mathrm{~atm} \times \frac{22.4 \mathrm{~L} / \mathrm{mol}}{30.0 \mathrm{~L} / \mathrm{mol}}=0.747 \mathrm{~atm}$
(b) $\left[\mathrm{SbCl}_{3}\right]=\left[\mathrm{Cl}_{2}\right]=(0.0200 \mathrm{~mol} / \mathrm{L})(0.292)$
$=5.84 \times 10^{-3} \mathrm{M}$
$\left[\mathrm{SbCl}_{5}\right]=(0.0200 \mathrm{~mol} / \mathrm{L})(0.708)=1.42 \times 10^{-2} \mathrm{M}$
$\mathrm{K}_{\mathrm{c}}=\frac{\left[\mathrm{SbCl}_{3}\right]\left[\mathrm{Cl}_{2}\right]}{\left[\mathrm{SbCl}_{5}\right]}=\frac{\left(5.84 \times 10^{-3}\right)^{2}}{1.42 \times 10^{-2}}=2.41 \times 10^{-3}$

## OR

$\mathrm{P}_{\mathrm{SbCl} 3}=\mathrm{P}_{\mathrm{C} 12}=(0.747 \mathrm{~atm})(0.292)=0.218 \mathrm{~atm}$
$\left.\mathrm{P}_{\mathrm{SbCl5}}=0.747 \mathrm{~atm}\right)(0.708)=0.529 \mathrm{~atm}$
$K_{p}=\frac{\left(\mathrm{P}_{\mathrm{SbCl}_{3}}\right)\left(\mathrm{P}_{\mathrm{Cl}_{2}}\right)}{\mathrm{P}_{\mathrm{SbCl}_{5}}}=\frac{(0.218)^{2}}{0.529}=8.98 \times 10^{-2}$
(c) $\mathrm{K}=\frac{\left\lfloor\mathrm{SbCl}_{3}\right\rfloor\left\lfloor\mathrm{Cl}_{2}\right\rfloor}{\left[\mathrm{SbCl}_{5}\right]}=0.117$
$\left[\mathrm{SbCl}_{5}\right]_{\text {equil. }}=\frac{(1.00-\mathrm{U} . / \mathrm{U}) \mathrm{mol}}{2.00 \mathrm{~L}}=0.15 \mathrm{M}$
$\left[\mathrm{SbCl}_{3}\right]_{\text {equil. }}=\frac{0.700 \mathrm{~mol}}{2.00 \mathrm{~L}}=0.350 \mathrm{M}$

# Equilibrium 

$\left[\mathrm{Cl}_{2}\right]_{\text {equil. }}=X \mathrm{M}$
$\mathrm{K}_{\mathrm{C}}=\frac{(\mathrm{U} .35 \mathrm{U})(\mathrm{X})}{0.15}=0.117 ; \mathrm{X}=0.050 \mathrm{M}=\left[\mathrm{Cl}_{2}\right]$
Moles $\mathrm{Cl}_{2(\text { equil. })}=(0.0050 \mathrm{~mol} / \mathrm{L})(2.00 \mathrm{~L})$
$=0.10 \mathrm{~mol} \mathrm{Cl}_{2}$
Moles $\mathrm{Cl}_{2}$ needed to make 0.300 mol SbCl 3 into $\mathrm{SbCl}_{5}=0.30 \mathrm{~mol}$
Moles $\mathrm{Cl}_{2}$ that must be added $=0.40 \mathrm{~mol}$
1988 D
$\mathrm{NH}_{4} \mathrm{HS}(s) \leftrightarrow \mathrm{NH}_{3}(g)+\mathrm{H}_{2} \mathrm{~S}(g) \quad \Delta \mathrm{H}^{\mathrm{o}}=+93$ kilojoules
The equilibrium above is established by placing solid $\mathrm{NH}_{4} \mathrm{HS}$ in an evacuated container at $25^{\circ} \mathrm{C}$. At equilibrium, some solid $\mathrm{NH}_{4} \mathrm{HS}$ remains in the container. Predict and explain each of the following.
(a) The effect on the equilibrium partial pressure of $\mathrm{NH}_{3}$ gas when additional solid $\mathrm{NH}_{4} \mathrm{HS}$ is introduced into the container
(b) The effect on the equilibrium partial pressure of $\mathrm{NH}_{3}$ gas when additional solid $\mathrm{H}_{2} \mathrm{~S}$ is introduced into the container
(c) The effect on the mass of solid $\mathrm{NH}_{4} \mathrm{HS}$ present when the volume of the container is decreased
(d) The effect on the mass of solid $\mathrm{NH}_{4} \mathrm{HS}$ present when the temperature is increased.

Answer:
(a) The equilibrium pressure of $\mathrm{NH}_{3}$ gas would be unaffected. $K_{P}=\left(\mathrm{P}_{\mathrm{NH} 3}\right)\left(\mathrm{P}_{\mathrm{H} 2 \mathrm{~S}}\right)$. Thus the amount of solid $\mathrm{NH}_{4} \mathrm{HS}$ present does not affect the equilibrium.
(b) The equilibrium pressure of $\mathrm{NH}_{3}$ gas would decrease. In order for the pressure equilibrium constant, $\mathrm{K}_{\mathrm{P}}$, to remain constant, the equilibrium pressure of $\mathrm{NH}_{3}$ must decrease when the pressure of $\mathrm{H}_{2} \mathrm{~S}$ is increased. $\mathrm{K}_{\mathrm{P}}=$ $\left(\mathrm{P}_{\mathrm{NH} 3}\right)\left(\mathrm{P}_{\mathrm{H} 2 \mathrm{~S}}\right)$. (A complete explanation based on LeChatelier's principle is also acceptable.)
(c) The mass of $\mathrm{NH}_{4} \mathrm{HS}$ increases. A decrease in volume causes the pressure of each gas to increase. To maintain the value of the pressure equilibrium constant, $\mathrm{K}_{\mathrm{p}}$, the pressure of each of the gases must decrease. The decrease is realized by the formation of more solid $\mathrm{NH}_{4} \mathrm{HS} . \mathrm{K}_{\mathrm{p}}=\left(\mathrm{P}_{\mathrm{NH} 3}\right)\left(\mathrm{P}_{\mathrm{H} 2 \mathrm{~S}}\right)$. (A complete explanation based on LeChatelier's principle is also acceptable.)
(d) The mass of $\mathrm{NH}_{4} \mathrm{HS}$ decreases because the endothermic reaction absorbs heat and goes nearer to completion (to the right) as the temperature increases.

1992 A

$$
2 \mathrm{NaHCO}_{3}(s) \leftrightarrow \mathrm{Na}_{2} \mathrm{CO}_{3}(\mathrm{~s})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g})+\mathrm{CO}_{2}(\mathrm{~g})
$$

Solid sodium hydrogen carbonate, $\mathrm{NaHCO}_{3}$, decomposes on heating according to the equation above.
(a) A sample of 100 . grams of solid $\mathrm{NaHCO}_{3}$ was placed in a previously evacuated rigid 5.00 -liter container and heated to $160^{\circ} \mathrm{C}$. 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 $\mathrm{H}_{2} \mathrm{O}(\mathrm{g})$ 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, $\mathrm{K}_{\mathrm{P}}$, and calculate its value for the reaction under the conditions in (a).
(d) If 110. grams of solid $\mathrm{NaHCO}_{3}$ had been placed in the 5.00 -liter container and heated to $160^{\circ} \mathrm{C}$, what would the total pressure have been at equilibrium? Explain.
Answer:

## Equilibrium

(a) $\mathrm{n}_{\text {gas }}=\frac{\mathrm{PV}}{\mathrm{RT}}=\frac{(1 . / 6 \mathrm{~atm})(5.00 \mathrm{~L})}{\left(0.0821 \frac{\mathrm{~L}-\mathrm{tm}}{\mathrm{mol} \_\mathrm{K}}\right)(433 \mathrm{~K})}=1.09 \mathrm{~mol}$
$\mathrm{mol} \mathrm{H} \mathrm{H}_{2} \mathrm{O}=(1 / 2)(1.09 \mathrm{~mol})=0.545 \mathrm{~mol} \mathrm{H}_{2} \mathrm{O}(g)$
(b) $0.545 \mathrm{~mol} \mathrm{H}_{2} \mathrm{O} \times \frac{2 \mathrm{~mol} \mathrm{NaHCO}_{3}}{1 \mathrm{~mol} \mathrm{H}_{2} \mathrm{O}} \times \frac{84.0 \mathrm{gNaHCO}_{3}}{1 \mathrm{~mol}}=91.9 \mathrm{~g} \mathrm{NaHCO}_{3}$ decomposed remaining $=100 . \mathrm{g}-91.6 \mathrm{~g}=8.4 \mathrm{~g}$
OR
$100-\left(0.545 \mathrm{~mol} \mathrm{H}_{2} \mathrm{O} \times \frac{18.0 \mathrm{~g}}{1 \mathrm{~mol}}+0.545 \mathrm{~mol} \mathrm{CO}_{2} \times \frac{44.0 \mathrm{~g}}{1 \mathrm{~mol}}\right)$
$=100 \mathrm{~g}-33.8 \mathrm{~g}=66 \mathrm{~g}($ or 66.2 g$)$ [includes $\mathrm{Na}_{2} \mathrm{CO}_{3}$ solid in this mass]
(c) $K_{p}=\left(\mathrm{P}_{\mathrm{H} 2 \mathrm{O}}\right)\left(\mathrm{P}_{\mathrm{CO} 2}\right)=(3.88)(3.88) \mathrm{atm}^{2}=15.1 \mathrm{~atm}^{2}$
(d) Pressure would remain at 7.76 atm . Since some solid remained when $100 . \mathrm{g}$ was used (and there has been no temperature change), then using 110 g will not affect the equilibrium.

1994 A

$$
\mathrm{MgF}_{2}(s) \leftrightarrow \mathrm{Mg}^{2+}(a q)+2 \mathrm{~F}^{-}(a q)
$$

In a saturated solution of $\mathrm{MgF}_{2}$ at $18^{\circ} \mathrm{C}$, the concentration of $\mathrm{Mg}^{2+}$ is $1.21 \times 10^{-3}$ molar. The equilibrium is represented by the equation above.
(a) Write the expression for the solubility-product constant, $K_{s p}$, and calculate its value at $18^{\circ} \mathrm{C}$.
(b) Calculate the equilibrium concentration of $\mathrm{Mg}^{2+}$ in 1.000 liter of saturated $\mathrm{MgF}_{2}$ solution at $18^{\circ} \mathrm{C}$ 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 $\mathrm{MgF}_{2}$ will form when 100.0 milliliters of a $3.00 \times 10^{-3}-\mathrm{molar} \mathrm{Mg}\left(\mathrm{NO}_{3}\right)_{2}$ solution is mixed with 200.0 milliliters of a $2.00 \times 10^{-3}$-molar NaF solution at $18^{\circ} \mathrm{C}$. Calculations to support your prediction must be shown.
(d) At $27^{\circ} \mathrm{C}$ the concentration of $\mathrm{Mg}^{2+}$ in a saturated solution of $\mathrm{MgF}_{2}$ is $1.17 \times 10^{-3}$ molar. Is the dissolving of $\mathrm{MgF}_{2}$ in water an endothermic or an exothermic process? Give an explanation to support your conclusion.
Answer:
(a) $K_{s p}=\left[\mathrm{Mg}^{2+}\right]\left[\mathrm{F}^{-}\right]^{2}=\left(1.21 \times 10^{-3}\right)\left(2.42 \times 10^{-3}\right)^{2}$
$=7.09 \times 10^{-9}$
(b) $X=$ concentration loss by $\mathrm{Mg}^{2+}$ ion
$2 X=$ concentration loss by $\mathrm{F}^{-}$ion
$\left[\mathrm{Mg}^{2+}\right]=\left(1.21 \times 10^{-3}-X\right) \mathrm{M}$
$\left[\mathrm{F}^{-}\right]=\left(0.100+2.42 \times 10^{-3}-2 X\right) \mathrm{M}$
since $X$ is a small number then $\left(0.100+2.42 \times 10^{-3}-2 X\right) \approx 0.100$
$K_{s p}=7.09 \times 10^{-9}=\left(1.21 \times 10^{-3}-X\right)(0.100)^{2}$
$X=1.2092914 \times 10^{-3}$
$\left[\mathrm{Mg}^{2+}\right]=1.21 \times 10^{-3}-1.20929 \times 10^{-3}=7.09 \times 10^{-7} \mathrm{M}$
(c) $\left[\mathrm{Mg}^{2+}\right]=3.00 \times 10^{-3} \mathrm{M} \times 100.0 \mathrm{~mL} / 300.0 \mathrm{~mL}=1.00 \times 10^{-3} \mathrm{M}$
$\left[\mathrm{F}^{-}\right]=2.00 \times 10^{-3} \mathrm{M} \times 200.0 \mathrm{~mL} / 300.0 \mathrm{~mL}=1.33 \times 10^{-3} \mathrm{M}$
trial $K_{s p}=\left(1.00 \times 10^{-3}\right)\left(1.33 \times 10^{-3}\right)^{2}=1.78 \times 10^{-9}$

## Equilibrium

trial $K_{s p}<=7.09 \times 10^{-9}, \therefore$ no ppt.
(d) @ $18^{\circ} \mathrm{C}, 1.21 \times 10^{-3} \mathrm{M} \mathrm{MgF}_{2}$ dissolves
(a) $27^{\circ} \mathrm{C}, 1.17 \times 10^{-3} \mathrm{M} \mathrm{MgF}_{2}$ dissolves
$\mathrm{MgF}_{2} \leftrightarrow \mathrm{Mg}^{2+}+2 \mathrm{~F}^{-}+$heat
dissolving is exothermic; if heat is increased it forces the equilibrium to shift left (according to LeChatelier's Principle) and less $\mathrm{MgF}_{2}$ will dissolve.

1995 A

$$
\mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g}) \leftrightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})+\mathrm{CO}(\mathrm{~g})
$$

When $\mathrm{H}_{2}(g)$ is mixed with $\mathrm{CO}_{2}(g)$ at $2,000 \mathrm{~K}$, equilibrium is achieved according to the equation above. In one experiment, the following equilibrium concentrations were measured.

$$
\begin{aligned}
{\left[\mathrm{H}_{2}\right] } & =0.20 \mathrm{~mol} / \mathrm{L} \\
{\left[\mathrm{CO}_{2}\right] } & =0.30 \mathrm{~mol} / \mathrm{L} \\
{\left[\mathrm{H}_{2} \mathrm{O}\right]=[\mathrm{CO}] } & =0.55 \mathrm{~mol} / \mathrm{L}
\end{aligned}
$$

(a) What is the mole fraction of $\mathrm{CO}(g)$ 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 $2,000 \mathrm{~K}$ to a lower temperature, 30.0 percent of the $\mathrm{CO}(\mathrm{g})$ is converted back to $\mathrm{CO}_{2}(\mathrm{~g})$. Calculate the value of $K_{c}$ at this lower temperature.
(e) In a different experiment, 0.50 mole of $\mathrm{H}_{2}(\mathrm{~g})$ is mixed with 0.50 mole of $\mathrm{CO}_{2}(\mathrm{~g})$ in a 3.0 -liter reaction vessel at $2,000 \mathrm{~K}$. Calculate the equilibrium concentration, in moles per liter, of $\mathrm{CO}(\mathrm{g})$ at this temperature.
Answer:
(a) $\mathrm{CO}=\mathrm{f}(0.55 \mathrm{~mol}, 1.6 \mathrm{~mol})=0.34$
(b) $K_{c}=\left(\left[\mathrm{H}_{2} \mathrm{O}\right][\mathrm{CO}]\right) /\left(\left[\mathrm{H}_{2}\right]\left[\mathrm{CO}_{2}\right]\right)=(0.55 \times 0.55) /(0.20 \times 0.30)=5.04$
(c) since $\Delta \mathrm{n}=0, K_{c}=K_{p}$
(d) $[\mathrm{CO}]=0.55-30.0 \%=0.55-0.165=0.385 \mathrm{M}$
$\left[\mathrm{H}_{2} \mathrm{O}\right]=0.55-0.165=0.385 \mathrm{M}$
$\left[\mathrm{H}_{2}\right]=0.20+0.165=0.365 \mathrm{M}$
$\left[\mathrm{CO}_{2}\right]=0.30+0.165=0.465 \mathrm{M}$
$\mathrm{K}=(0.385)^{2} /(0.365 \times 0.465)=0.87$
(e) let $X=\Delta\left[\mathrm{H}_{2}\right]$ to reach equilibrium
$\left[\mathrm{H}_{2}\right]=0.50 \mathrm{~mol} / 3.0 \mathrm{~L}-\mathrm{X}=0.167-X$
$\left[\mathrm{CO}_{2}\right]=0.50 \mathrm{~mol} / 3.0 \mathrm{~L}-\mathrm{X}=0.167-X$
$[\mathrm{CO}]=+X ;\left[\mathrm{H}_{2} \mathrm{O}\right]=+X$
$\mathrm{K}=X^{2} /(0.167-X)^{2}=5.04 ; X=[\mathrm{CO}]=0.12 \mathrm{M}$
1998 D
$\mathrm{C}(\mathrm{s})+\mathrm{H}_{2} \mathrm{O}_{(g)} \leftrightarrow \mathrm{CO}_{(g)}+\mathrm{H}_{2}(\mathrm{~g}) \quad \Delta H^{o}=+131 \mathrm{~kJ}$
A rigid container holds a mixture of graphite pellets $\left(\mathrm{C}(\mathrm{s}), \mathrm{H}_{2} \mathrm{O}(\mathrm{g}), \mathrm{CO}(\mathrm{g})\right.$, and $\mathrm{H}_{2}(\mathrm{~g})$ at equilibrium. State whether the number of moles of $\mathrm{CO}_{(g)}$ in the container will increase, decrease, or remain the same after each of the fol-

## Equilibrium

lowing 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 $\mathrm{H}_{2}(g)$ 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.

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, $\therefore$, 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 Required

1. $2 \mathrm{H}_{2} \mathrm{~S}(\mathrm{~g}) \rightarrow 2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{S}_{2(\mathrm{~g})}$

When heated, hydrogen sulfide gas decomposes according to the equation above. A 3.40 g sample of $\mathrm{H}_{2} \mathrm{~S}(\mathrm{~g})$ is introduced into an evacuated rigid 1.25 L container. The sealed container is heated to 483 K , and $3.72 \times 10^{-2} \mathrm{~mol}$ of $\mathrm{S}_{2(g)}$ is present at equilibrium.
(a) Write the expression for the equilibrium constant, $K_{\mathrm{c}}$, for the decomposition reaction represented above.
(b) Calculate the equilibrium concentration, in mol $\mathrm{L}^{-1}$, of the following gases in the container at 483 K .
(i) $\mathrm{H}_{2(g)}$
(ii) $\mathrm{H}_{2} \mathrm{~S}(\mathrm{~g})$
(c) Calculate the value of the equilibrium constant, $K_{\mathrm{c}}$, for the decomposition reaction at 483 K .
(d) Calculate the partial pressure of $\mathrm{S}_{2(\mathrm{~g})}$ in the container at equilibrium at 483 K .
(e) For the reaction $\mathrm{H}_{2(g)}+\frac{1}{2} \mathrm{~S}_{2(g)} \rightarrow \mathrm{H}_{2} \mathrm{~S}_{(g)}$ at 483 K , calculate the value of the equilibrium constant, $K_{\mathrm{c}}$.

Answer:
(a) $K_{\mathrm{c}}=\frac{\left[\mathrm{H}_{2}\right]^{2}\left[\mathrm{~S}_{2}\right]}{\left[\mathrm{H}_{2} \mathrm{~S}\right]^{2}}$
(b) (i) $\frac{3.72 \times 10^{-2} \mathrm{~mol} \mathrm{~S}_{2}}{1.25 \mathrm{~L}} \times \frac{2 \mathrm{~mol} \mathrm{H}_{2}}{1 \mathrm{~mol} \mathrm{~S}_{2}}=5.95 \times 10^{-2} M \mathrm{H}_{2}$
(ii) $\frac{\left(3.40 \mathrm{~g} \mathrm{H}_{2} \mathrm{~S} \times \frac{1 \mathrm{~mol}}{34.0 \mathrm{~g}}\right)-\left(3.72 \times 10^{-2} \mathrm{~mol} \mathrm{~S}_{2} \times \frac{2 \mathrm{~mol} \mathrm{H}_{2} \mathrm{~S}}{1 \mathrm{~mol} \mathrm{~S}_{2}}\right)}{1.25 \mathrm{~L}}=2.05 \times 10^{-2} \mathrm{M} \mathrm{H}_{2} \mathrm{~S}$

## Equilibrium

(c) $K_{\mathrm{c}}=\frac{\left[5.952 \times 10^{-2}\right]^{2}\left[\frac{3.72 \times 10^{-2}}{1.25}\right]}{[0.02048]^{2}}=0.251$
(d) $\mathrm{PV}=\mathrm{nRT}=1.18$
(e) $K^{\prime}{ }_{\mathrm{c}}=\sqrt{1 / K_{c}}=2.00$

