1. Hydrogen iodide is a stronger acid than HCl and is produced according to the equation $\mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g})--->2 \mathrm{HI}(\mathrm{g})$.
a. A partial equilibrium constant expression for this reaction is given. What is the numerical value of $x, y$, and $z$ ?
$\mathrm{K}_{\mathrm{eq}}=[\mathrm{HI}]^{\mathrm{x}} /\left[\mathrm{H}_{2}\right]^{\mathrm{y}}\left[\mathrm{I}_{2}\right]^{\mathrm{z}}$
b. $\mathrm{K}_{\mathrm{eq}}=64$ at $400^{\circ} \mathrm{C}$. Will there be more HI present at equilibrium or more $\mathrm{H}_{2}$ and $\mathrm{I}_{2}$ ? Give reasons.
c. LeChatelier's application:

If more $\mathrm{H}_{2}$ is added the reaction shifts toward products. In other words, more products are produced to re-establish equilibrium.
Add $\mathrm{H}_{2}$ so $[\mathrm{HI}]^{2} /\left[\mathrm{H}_{2}\right]\left[\mathrm{I}_{2}\right]$ decreases below $\mathrm{K}_{\text {eq }}=64$. To get the ratio of $[\mathrm{HI}]^{2} /\left[\mathrm{H}_{2}\right]\left[\mathrm{I}_{2}\right]$ back to 64 , the reaction has to form more products (numerator) so the reaction shifts towards products.
(i) If $\mathrm{HI}(\mathrm{g})$ is added, the reaction shifts to make more reactants (goes in reverse direction). Does the ratio of $[\mathrm{HI}]^{2} /\left[\mathrm{H}_{2}\right]\left[I_{2}\right]$ increase or decrease? To get this ratio back to 64, does the numerator or denominator have to decrease?
(ii) If $\mathrm{HI}(\mathrm{g})$ is removed, does the ratio of $[\mathrm{HI}]^{2} /\left[\mathrm{H}_{2}\right]\left[\mathrm{I}_{2}\right]$ increase or decrease? To get this ratio back to 64 , does the numerator or denominator have to decrease? Which direction does the reaction shift?
(iii) If $\mathrm{I}_{2}(\mathrm{~g})$ is added, does the ratio of $[\mathrm{HI}]^{2} /\left[\mathrm{H}_{2}\right]\left[\mathrm{I}_{2}\right]$ increase or decrease? To get this ratio back to 64 , does the numerator or denominator have to decrease? Which direction does the reaction shift?
(iv) If $\mathrm{H}_{2}(\mathrm{~g})$ is removed, does the ratio of $[\mathrm{HI}]^{2} /\left[\mathrm{H}_{2}\right]\left[\mathrm{I}_{2}\right]$ increase or decrease? To get this ratio back to 64 , does the numerator or denominator have to decrease? Which direction does the reaction shift?
(v) If the reaction pressure is raised, the reaction will not shift to either side. An increase in pressure is like an increase in concentration of each gas. Explain why an increase in pressure does shift the reaction.
d. $\Delta \mathrm{H}$ for this reaction is $-9.4 \mathrm{~kJ} /$ mole. If the reaction temperature is raised, will reaction shift to reactants or products?
(Hint: is this reaction exothermic or endothermic? Is heat a reactant or product in this reaction? If the reaction temperature increases, think of it as adding heat.)
e. If the reaction temperature is raised, the numerical value of K decreases. Explain why K decreases. (Hint: relate your answer to part d.)
f. Equilibrium calculation: 1 mole of $\mathrm{H}_{2}$ and 1 mole of $\mathrm{I}_{2}$ are placed in a 1 liter container at $400^{\circ} \mathrm{C}$. The reaction occurs.

Calculate the equilibrium concentrations of each reactant and product.

|  | $\mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g})$ | $---->$ | $2 \mathrm{HI}(\mathrm{g})$ |
| :--- | :--- | :---: | :--- |
| initial | 1 | 1 | 0 |
| reacts | $x$ | $x$ | $2 x$ |
| equilibrium | $1-x$ | $1-x$ | $2 x$ |

Substitute into $\mathrm{K}_{\mathrm{eq}}$ expression from Question 1a: $\mathrm{K}_{\mathrm{eq}}=64=[\mathrm{HI}]^{2} /\left[\mathrm{H}_{2}\right]\left[\mathrm{I}_{2}\right]=(2 \mathrm{x})^{2} /(1-\mathrm{x})(1-\mathrm{x})$
Solve for $x$ : $\quad 64(1-x)(1-x)=4 x^{2}$

$$
60 x^{2}-128 x+64=0
$$

Use quadratic equation: $\quad x=1.3$ and 0.8
$x$ can't be 1.3 because $\left[\mathrm{H}_{2}\right]$ and $\left[\mathrm{I}_{2}\right]$ would be less than 0 at equilibrium.
So $x=0.8$, which means $\left[\mathrm{H}_{2}\right]=1-0.8=0.2$ and $\left[\mathrm{I}_{2}\right]=1-0.8=0.2$ and $[\mathrm{HI}]=2(0.8)=1.6$ at equilibrium.
This makes sense since $\mathrm{K}_{\mathrm{eq}}=64$, there should be more products than reactants.
Answers:
a. $x=2, y=1, z=1$ from the coefficients in the balanced chemical equation.
b. More HI present at equilibrium because K is greater than 1 (more products and less reactants).
c. (i) When HI is added, ratio of $[\mathrm{HI}]^{2} /\left[\mathrm{H}_{2}\right]\left[\mathrm{I}_{2}\right]$ increases.

To get ratio back to 64, numerator has to decrease. This means HI reacts to form $\mathrm{H}_{2}$ and $\mathrm{I}_{2}$.
(ii) When HI is removed, ratio of $[\mathrm{HI}]^{2} /\left[\mathrm{H}_{2}\right]\left[\mathrm{I}_{2}\right]$ decreases.

To get ratio back to 64, denominator has to decrease. This means $\mathrm{H}_{2}$ and $\mathrm{I}_{2}$ react to form HI .
(iii) When $\mathrm{I}_{2}$ is added, ratio of $[\mathrm{HI}]^{2} /\left[\mathrm{H}_{2}\right]\left[\mathrm{I}_{2}\right]$ decreases.

To get ratio back to 64, denominator has to decrease. This means $\mathrm{H}_{2}$ and $\mathrm{I}_{2}$ react to form HI .
(iv) When $\mathrm{H}_{2}$ is removed, ratio of $[\mathrm{HI}]^{2} /\left[\mathrm{H}_{2}\right]\left[\mathrm{I}_{2}\right]$ increases.

To get ratio back to 64 , numerator has to decrease. This means HI reacts to form $\mathrm{H}_{2}$ and $\mathrm{I}_{2}$.
(v) If the reaction pressure is raised, the reaction will not shift to either side because there are the same number of moles of gas reactants and gas products. The stress of increasing pressure is only relieved by shifting the equiibrium reaction to the side with fewer moles of gas.
d. $\Delta \mathrm{H}$ for this reaction is $-9.4 \mathrm{~kJ} /$ mole, which means the reaction is exothermic. This tells us heat is a product. If the reaction temperature is raised, the reaction will shift to the reactant side. Raising the temperature produces less products and lowers the \% yield of products.
e. If the reaction temperature is raised, the numerical value of $K$ decreases because higher temperature shifts the reaction toward reactants and decreases K (less products and more reactants).
2. Hydrogen iodide decomposes according to the equation $2 \mathrm{HI}(\mathrm{g})--->\mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g})$.
a. Write an equilibrium constant expression for this reaction: $\mathrm{K}_{\mathrm{eq}}=$
b. $\mathrm{K}_{\text {eq }}=0.0156$ at $400^{\circ} \mathrm{C}$. Will there be more HI present at equilibrium or more $\mathrm{H}_{2}$ and $\mathrm{I}_{2}$ ? Give reasons.
c. LeChatelier's application:
(i) If $\mathrm{H}_{2}(\mathrm{~g})$ is removed, which direction does the reaction shift?
(ii) If the reaction pressure is raised, which direction does the reaction shift?
d. $\Delta \mathrm{H}$ for this reaction is $9.4 \mathrm{~kJ} / \mathrm{mole}$. If the reaction temperature is raised, will reaction shift to reactants or products?
$e$. If the reaction temperature is raised, will K increase or decrease?
f. Equilibrium calculation: 1 mole of HI is placed in a 1 liter container at $400^{\circ} \mathrm{C}$. The reaction occurs. Calculate the equilibrium concentrations of each reactant and product.
$2 \mathrm{HI}(\mathrm{g})--->\quad \mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g})$.
initial 1
reacts
equilibrium
Answers:
a. $\mathrm{K}_{\mathrm{eq}}=\left[\mathrm{H}_{2}\right]\left[\mathrm{I}_{2}\right] /[\mathrm{HI}]^{2}$
b. $\mathrm{K}_{\text {eq }}=0.0156$ at $400^{\circ} \mathrm{C}$ means more HI present at equilibrium and less $\mathrm{H}_{2}$ and $\mathrm{I}_{2}$ because K is less than 1 .
c. (i) If $\mathrm{H}_{2}(\mathrm{~g})$ is removed, ratio of $\left[\mathrm{H}_{2}\right]\left[\mathrm{I}_{2}\right] /[\mathrm{HI}]^{2}$ decreases.

To get ratio back to 0.0156 , denominator has to increase. This means HI reacts to form $\mathrm{H}_{2}$ and $\mathrm{I}_{2}$ and reaction shifts to make more products.
(ii) If the reaction pressure is raised, the reaction will not shift to either side because there are the same number of moles of gas reactants and gas products. The stress of increasing pressure is only relieved by shifting the equiibrium reaction to the side with fewer moles of gas.
d. $\Delta \mathrm{H}$ for this reaction is $9.4 \mathrm{~kJ} /$ mole, which means the reaction is endothermic. This tells us heat is a reactant. If the reaction temperature is raised, the reaction will shift to the product side. Raising the temperature produces more products and raises the \% yield of products.
e. If the reaction temperature is raised, K increases because more products are produced (more products and less reactants increases K).
f. Equilibrium calculation: 1 mole of HI is placed in a 1 liter container at $400^{\circ} \mathrm{C}$. The reaction occurs. Calculate the equilibrium concentrations of each reactant and product.

|  | $2 \mathrm{HI}(\mathrm{g}) \cdots$ | $\mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g})$. |  |
| :--- | :--- | :--- | :--- |
| initial | 1 | 0 | 0 |
| reacts | $x$ | $0.5 x$ | $0.5 x$ |
| equilibrium | $1-x$ | $0.5 x$ | $0.5 x$ |

Substitute into $\mathrm{K}_{\mathrm{eq}}$ expression from Question 2a: $\mathrm{K}_{\mathrm{eq}}=0.0156=\left[\mathrm{H}_{2}\right]\left[\mathrm{I}_{2}\right] /[\mathrm{HI}]^{2}=(0.5 \mathrm{x})(0.5 \mathrm{x}) /(1-\mathrm{x})^{2}$
$\begin{array}{ll}\text { Solve for } x: \quad & 0.0156\left(1-2 x+x^{2}\right)=0.25 x^{2} \\ & 0.2344 x^{2}-0.0312 x+0.0156=0\end{array}$
Use quadratic equation: $\quad x=0.199872$ and -0.332978
$x$ can't be -0.332978 because $\left[\mathrm{H}_{2}\right]$ and $\left[\mathrm{I}_{2}\right]$ would be less than 0 at equilibrium.
So $x=0.199872$, which means $[\mathrm{HI}]=1-0.199872=0.800128=0.80 \mathrm{M}$
$\left[\mathrm{H}_{2}\right]=0.5(0.199872)=0.099936=0.10 \mathrm{M}$
and $\left[I_{2}\right]=0.5(0.199872)=0.099936=0.10 \mathrm{M}$ at equilibrium.
This makes sense since $\mathrm{K}_{\mathrm{eq}}=0.0156$, there should be more reactants than products.
3. Under the conditions of a car engine, nitrogren and oxygen reacts to form $\mathrm{NO}_{\mathrm{x}}$, which is a component of smog:

$$
\begin{aligned}
& \mathrm{N}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})-->2 \mathrm{NO}(\mathrm{~g}) \\
& \mathrm{N}_{2}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g})-->2 \mathrm{NO}_{2}(\mathrm{~g})
\end{aligned}
$$

a. For each reaction, write an equilibrium constant expression.
b. Under what temperature (low $T$ or high $T$ ) and pressure (low $P$ or high $P$ ) conditions does each reaction occur? Give reasons based on LeChatelier's principle.
Answers:
$\begin{array}{ll}\text { a. } \mathrm{N}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})-->2 \mathrm{NO}(\mathrm{g}) & \mathrm{K}_{\text {eq }}=[\mathrm{NO}]^{2} /\left[\mathrm{N}_{2}\right]\left[\mathrm{O}_{2}\right] \\ \mathrm{N}_{2}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g})-->2 \mathrm{NO}_{2}(\mathrm{~g}) & \mathrm{K}_{\text {eq }}=[\mathrm{NO}]^{2} /\left[\mathrm{N}_{2}\right]\left[\mathrm{O}_{2}\right]^{2}\end{array}$
b. $\mathrm{N}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})$--> $2 \mathrm{NO}(\mathrm{g}) \quad 2$ moles of gas reactants --> 2 moles of gas products so pressure does not affect equilibrium - reaction will not shift to reactants or products if $P$ is changed.
$\mathrm{N}_{2}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g})-->2 \mathrm{NO}_{2}(\mathrm{~g}) \quad 3$ moles of gas reactants --> 2 moles of gas products so increasing pressure will shift reaction to products side.
For effect of temperature, need to know if the reaction is exothermic $(\Delta \mathrm{H}<0)$ or endothermic $(\Delta \mathrm{H}>0)$.
Look up $\Delta \mathrm{H}$ of formation of each reactant and product and apply Hess' law (see Chem 1A).
$\mathrm{N}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})-->2 \mathrm{NO}(\mathrm{g}) \quad \Delta \mathrm{H}=90.4 \mathrm{~kJ} / \mathrm{mole}==>$ endothermic so heat is a reactant. Increasing temperature will shift reaction to products side.
$\mathrm{N}_{2}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g})-->2 \mathrm{NO}_{2}(\mathrm{~g}) \quad \Delta \mathrm{H}=33.9 \mathrm{~kJ} /$ mole $==>$ endothermic so heat is a reactant. Increasing temperature will shift reaction to products side.
4. Dinitrogen tetroxide, $\mathrm{N}_{2} \mathrm{O}_{4}$, is a colorless gas that boils at $21^{\circ} \mathrm{C}$. As a gas, it is extensively dissociated to $\mathrm{NO}_{2}$. As a liquid, it is partly dissociated to $\mathrm{NO}_{2} . \mathrm{NO}_{2}$ is a reddish-brown toxic gas that makes up part of the brown cloud in Southern California and Denver during the winter months. (Reddish-brown toxic $\mathrm{NO}_{2}$ gas gets trapped in lower atmosphere due to temperature inversion in winter in which less dense warm air traps more dense cold air beneath it.)
$\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g})$ <==> $2 \mathrm{NO}_{2}(\mathrm{~g})$
a. Write an equilibrium constant expression.
b. At $25^{\circ} \mathrm{C}, 1.00$ mole $\mathrm{N}_{2} \mathrm{O}_{4}$ is placed in a 1.0 liter container. At equilibrium, the container has $0.28 \mathrm{~mole} \mathrm{NO}_{2}$ present. Calculate a numerical value for $\mathrm{K}_{\text {eq }}$.
c. At $25^{\circ} \mathrm{C}$, the gas inside the container is reddish-brown. When this container is placed in an ice bath, the gas is colorless. Is the dissociation of $\mathrm{N}_{2} \mathrm{O}_{4}$ exothermic or endothermic? Explain. Calculate the heat of reaction to confirm your answer.
Answers:
a. $\mathrm{K}_{\mathrm{eq}}=\left[\mathrm{NO}_{2}\right]^{2} /\left[\mathrm{N}_{2} \mathrm{O}_{4}\right]$
b. $\quad \mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g}) \quad<==>2 \mathrm{NO}_{2}(\mathrm{~g})$
initial $\quad 1 \mathrm{moles} / 1 \mathrm{I}=1 \mathrm{M} \quad 0$
reacts $x \quad 2 x$
equilibrium $\quad 1-\mathrm{x} \quad 2 \mathrm{x}=0.1 \mathrm{moles} / 1 \mathrm{I}=0.28 \mathrm{M}$ so $\mathrm{x}=0.14 \mathrm{M}$
So at equilibrium, $\left[\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g})\right]=1-0.14 \mathrm{M}=0.86 \mathrm{M}$
$\mathrm{K}_{\mathrm{eq}}=\mathrm{K}_{\mathrm{eq}}=\left[\mathrm{NO}_{2}\right]^{2} /\left[\mathrm{N}_{2} \mathrm{O}_{4}\right]=[0.28]^{2} /[0.86]=0.09$
c. At $25^{\circ} \mathrm{C}$, the gas inside the container is reddish-brown $==>$ this tells us $\mathrm{NO}_{2}(\mathrm{~g})$ is present.

When this container is placed in an ice bath, the gas is colorless ==> this tells us $\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g})$ is present.
When placed in an ice bath, reaction shifts to reactant side.
For reaction to shift to reactant side when heat is removed, heat has to be a reactant ==> dissociation of $\mathrm{N}_{2} \mathrm{O}_{4}$ endothermic.
Calculate the heat of reaction $==>$ look up $\Delta \mathrm{H}$ of formation of each reactant and product and apply Hess' law (see Chem 1A). $\Delta \mathrm{H}=58.2 \mathrm{~kJ} / \mathrm{mole}==>$ endothermic
5. The Haber process is the industrial process for the synthesis of ammonia $\left(\mathrm{NH}_{3}\right)$ from $\mathrm{N}_{2}$ and $\mathrm{H}_{2}$. In this process, the reaction conditions are high pressure and low temperature. A catalyst is used and product is removed from the reaction vessel during the reaction.
a. Write a balanced chemical equation that represents this reaction.
b. Write an equilibrium constant expression.
c. Explain why these reaction conditions (high pressure, low temperature, catalyst is used, and product is removed) are used. If a catalyst was not used, could a higher reaction be used to optimize the yield? Give reasons.
Answers:
a. $\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g})-->2 \mathrm{NH}_{3}(\mathrm{~g})$
b. $\mathrm{K}_{\text {eq }}=\left[\mathrm{NH}_{3}\right]^{2} /\left(\left[\mathrm{N}_{2}\right]\left[\mathrm{H}_{2}\right]^{3}\right)$
$\mathrm{K}_{\text {eq }}=1.6 \times 10^{-4}$ at $\mathrm{T}=400^{\circ} \mathrm{C}$.
c. High pressure: 4 moles gas reactants --> 2 moles gas products so raising the pressure shifts reaction to product side and increases the yield of $\mathrm{NH}_{3}$. This reaction runs at $\mathrm{P}=100 \mathrm{~atm}$.
Low temperature: Calculate the heat of reaction $==>$ look up $\Delta H$ of formation of each reactant and product and apply
Hess' law (see Chem 1A). $\Delta \mathrm{H}=-91.2 \mathrm{~kJ} / \mathrm{mole}==>$ exothermic so heat is a product. Lower temperature (remove heat)
shifts reaction to product side and increases the yield of $\mathrm{NH}_{3}$. Note: this reaction runs at $\mathrm{T}=400^{\circ} \mathrm{C}$ because the catalyst
requires a T of at least $400^{\circ} \mathrm{C}$ to be efficient.
A catalyst is used to make the reaction go faster.
Product is removed to shift reaction to product side and increase yield of $\mathrm{NH}_{3}$.
If a catalyst was not used, a higher reaction shifts the reaction to the reactant side and lowers the yield of $\mathrm{NH}_{3}$.
6. Drano drain cleaner consists of Al filings and NaOH pellets. When water is added, the heat produced melts and saponifies the fat that clogs a drain.

$$
2 \mathrm{Al}(\mathrm{~s})+2 \mathrm{NaOH}(\mathrm{~s})+6 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})-->2 \mathrm{NaAl}(\mathrm{OH}) 4(\mathrm{aq})+3 \mathrm{H}_{2}(\mathrm{~g})
$$

a. Write an equilibrium constant expression.
b. Would you expect this reaction to have a large K or small K ? Explain.
c. In terms of reactants and products, explain how this reaction can be shifted to the right (toward products).
d. If an excess amount of water is added, how will the reaction be affected?
e. If hot water was added instead of cold water, would Drano work better? In other words, which direction would the reaction shift?
f. If the drain was plugged immediately after Drano was added to the clog, would Drano work better? In other words, which direction would the reaction shift?
Answers:
a. $\mathrm{K}_{\mathrm{eq}}=[\mathrm{NaAl}(\mathrm{OH}) 4(\mathrm{aq})]^{2}\left[\mathrm{H}_{2}\right]^{3}$
$\mathrm{Al}(\mathrm{s}), \mathrm{NaOH}(\mathrm{s})$, and $\mathrm{H}_{2} \mathrm{O}(\mathrm{I})$ are pure substances to the concentration $=1$.
b. Large K because the reaction occurs ==> Drano works!
c. Reaction can be shifted to the right toward products by adding reactants or removing products.
d. Adding excess (more) amount of water shifts the reaction to the right to make more products.
e. This reaction is exothermic ("When water is added, the heat produced melts and saponifies the fat that clogs a drain.") so heat is a product. So using hot water (add more product (heat) shifts the reaction toward the reactant side ==> Drano will not work as well based on equilibrium. However, hot water makes the reaction go faster.
f. 0 moles gas reactants --> 3 moles gas products.

If the drain was plugged immediately after Drano was added to the clog, pressure increases and the reaction shifts toward the reactant side ==> Drano will not work as well based on equilibrium.
7. In Lab 1, an alcohol reacts with a carboxylic acid to produce an ester and water. This reaction is an exothermic, equilibrium reaction and is catalyzed with sulfuric acid.
a. Draw a reaction energy diagram for this reaction with and without the catalyst. Label $\Delta H$ and the activation energy on your diagram.
b. Two ways to increase the reaction rate are to raise the temperature and to use a catalyst. Why is a catalyst used in the esterification reaction instead of heating the reaction for an hour at $100^{\circ} \mathrm{C}$ ?
c. Draw a graph that shows the concentration of acid vs. time of reaction and the concentration of ester vs. time of reaction. What happens to the reaction rate as a reaction proceeds?
Answers:
a. See Objective 6 Quiz Practice Problem 1c. This reaction energy diagram shows the reaction of acetic acid + isoamyl alcohol to produce isoamyl acetate, which smells like banana.


Progress of Reaction
b. This reaction is exothermic (heat is a product) so raising the temperature shifts the reaction to the reactant side and lowers the yield of ester.
So a catalyst is used to make the reaction go faster rather than heating the reaction for an hour at $100^{\circ} \mathrm{C}$, which lowers the yield of ester.
c. Reaction rate decreases as the reaction proceeds.

See slope of tangent of line to curve. Slope = rate.
Rate of disappearance of acid is negative because [acid] decreases. Slope is negative and decreases with time.
Rate of appearance of ester is positive because [ester] increases. Slope is postive and decreases with time.


