## Chapter 9- Lecture Worksheet 1

1A. LA Smog is composed of nitrogen oxide emissions. Draw Lewis structures:

$$
2 \mathrm{NO}_{2}(\mathrm{~g})<----->\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g})
$$




Break no bonds $\left(\mathrm{E}_{\mathrm{in}}=0\right)$... Make one bond $\left(\mathrm{E}_{\text {out }}>0\right)$
EXOTHERMIC reaction
B. This reactions is: 1. ENDOTHERMIC 2. EXOTHERMIC 3. CANNOT TELL
C. At equilibrium:

1. $\left[\mathrm{NO}_{2}\right]=\left[\mathrm{N}_{2} \mathrm{O}_{4}\right]$
2. Both $1 \& 4$ are correct
3. $\left[\mathrm{NO}_{2}\right]^{2}=\left[\mathrm{N}_{2} \mathrm{O}_{4}\right]$
4. Both $2 \& 4$ are correct
5. $2\left[\mathrm{NO}_{2}\right]=\left[\mathrm{N}_{2} \mathrm{O}_{4}\right]$
6. Both $3 \& 4$ are correct
7. $\mathrm{k}_{\text {forward }}=\mathrm{k}_{\text {reverse }}$
8. Both $1 \& 5$ are correct
9. Rate $_{\text {forward }}=$ Rate $_{\text {reverse }}$

0 . $1,4 \& 5$ are all correct
D. Experimental data. Draw some conclusions:

| Initial | Concs (M) |
| :---: | :---: |
| $\left[\mathrm{NO}_{2}(\mathrm{~g})\right]_{0}$ | $\left[\mathrm{~N}_{2} \mathrm{O}_{4}(\mathrm{~g})\right]_{0}$ |
| $\mathbf{0 . 0 0 0}$ | $\mathbf{0 . 6 7 0}$ |
| 0.0500 | 0.445 |
| 0.0300 | 0.500 |
| 0.0400 | 0.600 |
| $\mathbf{0 . 2 0 0}$ | $\mathbf{0 . 0 0}$ |
| $\left[\mathrm{NO}_{2}(\mathrm{~g})\right]_{\mathrm{eq}}$ | $\left[\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g})\right]_{\mathrm{eq}}$ |
| $\mathbf{0 . 0 5 4 7}$ | $\mathbf{0 . 6 4 3}$ |
| 0.0457 | 0.448 |
| 0.0475 | 0.491 |
| 0.0523 | 0.594 |
| $\mathbf{0 . 0 2 0 4}$ | $\mathbf{0 . 0 8 9 8}$ |

## Ratios of Equilibrium Concentrations $\left(25^{\circ} \mathrm{C}\right)$

| $\frac{\left[\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g})\right]}{\left[\mathrm{NO}_{2}(\mathrm{~g})\right]}$ |
| :---: |
| 11.76 |
| 9.80 |
| 10.34 |
| 11.36 |
| 4.4 |

Start with different initial concentrations, always get more $\mathrm{N}_{2} \mathrm{O}_{4}$ than $\mathrm{NO}_{2}$ at equilibrium. Doesn't matter if start with all $\mathrm{NO}_{2}$ or all $\mathrm{N}_{2} \mathrm{O}_{4}$. Independent of direction.
Ratio $\left[\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g})\right] /\left[\mathrm{NO}_{2}(\mathrm{~g})\right]^{2}=$ constant.
E. Why does this work ? Assume a 1 step mechanism and find the ratio ( $\left.\mathbf{k}_{\text {forward }} / \mathbf{k}_{\text {reverse }}\right)$

Rate $_{\text {forward }}=$ Rate $_{\text {reverse }}$
$k_{\text {forward }}\left[\mathrm{NO}_{2}\right]^{2}=k_{\text {reverse }}\left[\mathrm{N}_{2} \mathrm{O}_{4}\right]$
$\left(\frac{k_{\text {forvard }}}{k_{\text {reverse }}}\right)=\frac{\left[\mathrm{N}_{2} \mathrm{O}_{4}\right]}{\left[\mathrm{NO}_{2}\right]^{2}}=$ Constan $t=K_{c} \ldots$ the Equilibrium Constant
2. Write equilibrium constant expression for:


For reaction $A$ at $25^{\circ} \mathrm{C}, \mathbf{K}_{\text {eq }}=\mathbf{3 . 5} \times 1 \mathbf{1 0}^{\mathbf{8}}$.
We can say that at equilibrium:

1. There is a lot of $\mathrm{NH}_{3}$ relative to $\mathbf{N}_{2}$ and $\mathbf{H}_{2}$

$$
K_{c}=\frac{\left[\mathrm{NH}_{3}\right]^{2}}{\left[N_{2}\right]\left[H_{2}\right]^{3}}
$$

2. There is a lot of $\mathrm{N}_{2}$ relative to $\mathrm{NH}_{3}$ and $\mathrm{H}_{2}$
3. There is a lot of $\mathrm{H}_{2}$ relative to $\mathrm{NH}_{3}$ and $\mathrm{N}_{2}$
4. There is about the same amount of $\mathrm{NH}_{3}$ as
$\mathrm{N}_{2}$ and $\mathrm{H}_{2}$
5. Cannot tell from the information given.
6. Write equilibrium constant expression for: $\quad$ For reaction $B$ at $25^{\circ} \mathrm{C}, \mathbf{K}_{\mathrm{eq}}=\mathbf{9 . 8} \times 1 \mathbf{1 0}^{-9}$.
$\mathrm{CaCO}_{3}(\mathrm{~s})<-\ldots \mathrm{Ca}^{2+}(\mathrm{aq})+\mathrm{CO}_{3}{ }^{2-}(\mathrm{aq})$

$$
K_{c}=\left[C a^{2+}(a q)\right]\left[C O_{3}^{2-}(a q)\right]
$$

Note: $\left[\mathrm{CaCO}_{3}(\mathrm{~s})\right]=$ constant
Do not include pure solids or pure liquids in K expression

We can say that:

1. $\mathrm{CaCO}_{3}(\mathrm{~s})$ is very soluble.
2. $\mathrm{CaCO}_{3}(\mathrm{~s})$ is not very soluble.
3. Cannot tell from the information given.
4. Write the equilibrium constant expression for: $\mathbf{2 N H}_{\mathbf{3}}(\mathrm{g})<----->\mathbf{N}_{\mathbf{2}}(\mathrm{g})+\mathbf{3} \mathbf{H}_{\mathbf{2}}(\mathrm{g})$

How is this related to the expression for K in question $\mathbf{2}$ above ?

$$
K_{4}=\frac{\left[N_{2}\right]\left[H_{2}\right]^{3}}{\left[N H_{3}\right]^{2}}=\mathbf{1} / \mathbf{K}_{2}
$$

5. Write the equilibrium constant expression for: $1 / 2 \mathbf{N}_{\mathbf{2}}(\mathrm{g})+\mathbf{3 / 2} \mathbf{H}_{\mathbf{2}}(\mathrm{g})<----->\mathbf{N H}_{3}(\mathrm{~g})$ How is this related to the expression for K in question $\mathbf{2}$ above ?

$$
K_{5}=\frac{\left[\mathrm{NH}_{3}\right]}{\left[\mathrm{N}_{2}\right]^{1 / 2}\left[\mathrm{H}_{2}\right]^{3 / 2}}=\left(\mathbf{K}_{2}\right)^{1 / 2}
$$

## 6. Conclusions ?

Reverse reaction - Take reciprocal of K
Multiply reaction by $\mathbf{n}$ - Raise K to power of $\mathbf{n}$

| PRS Answers |  |
| :--- | :--- |
| $1 . \mathrm{K}=\mathrm{K}_{\mathrm{A}}$ | $6 . \mathrm{K}=\left(\mathrm{K}_{\mathrm{A}}\right)^{2}$ |
| $2 . \mathrm{K}=\left(1 / \mathrm{K}_{\mathrm{A}}\right)$ | $7 . \mathrm{K}=\left(1 / \mathrm{K}_{\mathrm{A}}\right)^{1 / 2}$ |
| $3 . \mathrm{K}=2\left(1 / \mathrm{K}_{\mathrm{A}}\right)$ | 8. $\mathrm{K}=(1 / 2)\left(1 / \mathrm{K}_{\mathrm{A}}\right)^{1 / 2}$ |
| $4 . \mathrm{K}=2 \mathrm{~K}_{\mathrm{A}}$ | 9. $\mathrm{K}=\left(\mathrm{K}_{\mathrm{A}}\right)^{1 / 2}$ |
| $5 . \mathrm{K}=\left(1 / \mathrm{K}_{\mathrm{A}}\right)^{2}$ |  |

