1. \[ \text{[ratio } M \text{]}^a \text{[ratio } M \text{]}^b = \text{ratio of rates} \]

Using experiment 1 & 2 : \[ \text{[.1M/.1M]}^a \text{[.2M/.3M]}^b = 0.004 \text{ M/s/0.0135 M/s} \]
Since the A concentrations are equal we can cancel out that factor and:
\[ \text{[.2M/.3M]}^b = 0.004 \text{ M/s / 0.0135 M/s} \]
To solve algebracially : \[ b \log 0.667 = \log .296 \]
\[ b = 3 \]

If you don’t understand this process, go to the website home page and under Chemistry Help Topics choose Rate Law: Kinetics.

Using Exp. 2&4 : \[ \text{[.1M/.3M]}^b \text{[.3M/.4M]}^a = 0.0135 \text{ M/s / .288 M/s} \]
Since b did not stay constant in this problem, we must now substitute the power of 3 for b, so the second factor becomes : \[ \text{[.3M/.4M]}^3 \]
\[ \text{[.1M/.3M]}^a \text{[.3M/.4M]}^3 = [0.0135 \text{ M/s / 0.288 M/s}] \]

\[ [0.33]^a [0.75]^3 = 0.0469 \]
\[ 0.33^a = .111 \]
\[ a = 2 \] ( if you need help solving this see Rate Law: Kinetics)

Answer: Rate = \( k[A]^2 [B]^3 \)

2. For an elementary reaction (occurs in a single event) just use the coefficients in the balanced equation for the powers. So, the rate law is:
\[ R = k[\text{NO}_2]^2 \]
No calculations are required if the reaction is elementary

3. \( \ln [A]_0 / [A]_t = kt \)
\( \ln [1 \text{ atm}] / [0.803 \text{ atm}]_t = k (10,000s) \)
\[ 0.219 = 10000s k \]
\[ k = 2.2 \times 10^{-5} \text{ s}^{-1} \]

4. \( 1/ [A]_t - 1/ [A]_0 = kt \)
\[ 1/\text{[A]}_t = kt - 1/\text{[A]}_0 \]
\[ 1/\text{[A]}_t = (0.02 \text{ L mol}^{-1}\text{s}^{-1})(120\text{s}) + 1/\text{[0.2]} \]
\[ [A]_t = 0.14 \text{ M} \]
5. To prove first order and second order plot the following:

\[ \ln[A]_0/\ln[A] = kt \]
Plot the two things that change: \( \ln[A] \) vs t
To prove second order:
\[ 1/[A] - 1/[A]_0 = kt \]
plot \( 1/[A] \) vs t

6. \( \ln[A]_0/\ln[A] = kt \)
\[ \ln[100]/[35] = k \text{ 45 s} \]
\[ k = 0.0233 \text{ s}^{-1} \]
\[ t_{1/2} = \ln2 / k = 0.693 / 0.0233 \text{ s}^{-1} = 30 \text{ s} \]

7. \( \ln k_2/k_1 = -E_a/R \left[ 1/T_2 - 1/T_1 \right] \)
\[ \ln 100/10 = \frac{E_a}{8.314 \text{ J/mole K}} \left[ 1/400 - 1/300 \right] \]
\[ E_a = 23000 \text{ J or 23 kJ} \]

8. Work the problem with 1 and 0.5 to see what effect it has.
\[ R = k[P]^2 \]
\[ = k[1]^2 \]
\[ = k \]
\[ R = k[P]^2 \]
\[ = k[0.5]^2 \]
\[ = 0.25k \]
Therefore, it is decreased by 4.

9. (60 moles NH\textsubscript{3}/1) (6 mole H\textsubscript{2}O / 4 moles NH\textsubscript{3}) = 9 moles of H\textsubscript{2}O
This is a stoichiometric problem.

10. For a mechanism to be consistent it must meet two requirements. (a) The steps of the mechanism must add up to equal the overall reaction. (b) The rate determining step (slow step) must give you the derived rate law.
In this mechanism, the steps do add up to the overall reaction. In other words, the HI cancels because it is on the reactant side in one equation and the product side on the other. But, the slow step give the rate law: \( R = k[HI][ICl] \) which is not the derived rate law. HI is the intermediate. It is produced in one step and consumed in another step.

For more help go to website Chemistry Help Topics and open Kinetics: Mechanisms.)
11. bimolecular, intermediate, rate law: \( R = k[A_2][B_2] \) based on the slow step.

12. \( \text{L}^2/\text{mol}^2.\text{s} \)

13.

14. \[ R \quad 2A \quad + \quad B \rightarrow C \quad R = \text{reaction} \]

<table>
<thead>
<tr>
<th></th>
<th>( I )</th>
<th>( 0.6 )</th>
<th>( 0.8 )</th>
<th>( 0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C )</td>
<td>( -0.2 )</td>
<td>( -0.01 )</td>
<td>( +0.01 )</td>
<td></td>
</tr>
<tr>
<td>( E )</td>
<td>( 0.4 )</td>
<td>( 0.7 )</td>
<td>( 0.1 )</td>
<td></td>
</tr>
</tbody>
</table>

\( K = [C] / [A]^2 [B] = 0.1 / [0.4]^2 [0.7] = 0.893 \)

15. \[ R \quad 2H_2S \rightarrow 2H_2 \quad + \quad S_2 \]

<table>
<thead>
<tr>
<th></th>
<th>( I )</th>
<th>( 0.15 \text{ M} )</th>
<th>( 0 )</th>
<th>( 0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C )</td>
<td>( -1.62 \times 10^{-3} )</td>
<td>( +1.62 \times 10^{-3} )</td>
<td>( +8.1 \times 10^{-4} )</td>
<td></td>
</tr>
<tr>
<td>( E )</td>
<td>( 1.48 \times 10^{-1} )</td>
<td>( 1.62 \times 10^{-3} )</td>
<td>( 8.1 \times 10^{-4} )</td>
<td></td>
</tr>
</tbody>
</table>

\( K = [H_2]^2 [S_2] / [H_2S]^2 = [1.62 \times 10^{-3}]^2 [8.1 \times 10^{-4}] / [1.48 \times 10^{-1}] = 9.7 \times 10^{-8} \)

16. \[ R \quad 2HCN \rightarrow H_2 \quad + \quad C_2N_2 \]

<table>
<thead>
<tr>
<th></th>
<th>( I )</th>
<th>( 25 \text{ atm} )</th>
<th>( 0 )</th>
<th>( 0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C )</td>
<td>( -2x )</td>
<td>( x )</td>
<td>( x )</td>
<td></td>
</tr>
<tr>
<td>( E )</td>
<td>( 25-2x )</td>
<td>( x )</td>
<td>( x )</td>
<td></td>
</tr>
</tbody>
</table>

\( K = [x][x] / [25-2x]^2 \)

\( (4 \times 10^{-4})^{1/2} = (x^2 / [25-2x]^2)^{1/2} \quad (1/2 \text{ power means square root}) \)

\( 2 \times 10^{-2} = x / 25-2x \)
x = 0.48 atm = C₂N₂

17. \[ R \quad A \quad + \quad B \quad \rightarrow \quad 2C \]

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>1</th>
<th>1</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>x</td>
<td>x</td>
<td>-2x</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>1+x</td>
<td>1+x</td>
<td>1-2x</td>
<td></td>
</tr>
</tbody>
</table>

To decide which side is +x and which is -x requires the calculation of \( Q \) (Reaction Quotient).

\[
Q = \frac{[c]^2}{[A][B]} = \frac{[1]^2}{[1][1]} = 1
\]

\( Q = 1 \) and \( K = .25 \)

One method to determine which way the reaction shifts is to put \( Q \) and \( K \) on a number line.

\[
\begin{array}{ccccccc}
& 0 & .25 & 1 & 2 & 3 & 4 & 5 & 6 \\
\end{array}
\]

At the present time you are at \( Q \) concentration, so to go from \( Q \) (1) to \( K \) (.25) you must move to the left on the number line. This means the reaction will shift to the left and the left side will be the positive side.

\[
K(.25) = \frac{[C]^2}{[A][B]} = \frac{[1-2x]^2}{[1+x]^2}
\]

Taking the square root of both sides: \( .5 = 1-2x / 1+x \) and \( x = .2 \)

The concentration of \( C \) is \( 1-2x = 1-2(.2) = .6 \) M.

18. \[ R \quad HI \quad \rightarrow \quad H^+ \quad + \quad A^- \]

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>0.15</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>-x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>0.15-x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

\[
K = \frac{[H^+][A^-]}{[HA]}
\]
1.8 \times 10^{-5} = \frac{[x]^2}{0.15-x}

Since K is very small, we will ignore the x associated with the 0.15

1.8 \times 10^{-5} = \frac{x^2}{0.15}

x^2 = 2.7 \times 10^{-6}

x = 1.64 \times 10^{-3} = [H^+]

To determine if the x should have been ignored, we will calculate the % ionization or sometimes called the % dissociation.

In math, \% = \frac{\text{part}}{\text{total}} \times 100

= \frac{1.64 \times 10^{-3}}{0.15} \times 100 = 1.1 \% \text{ Therefore it was fine to ignore the x. If it is more than 5\%, then the x should not be ignored.}

Notice, the part will always be the value of x and the total is what you started with.

19. \ Q = \frac{[iso]}{[n]} = \frac{2.9}{1} = 2.9 \ (\text{remember Q is the same as K but using initial amounts in the expression for Q.})

Using a number line and the fact that K = 2.5

\[ 0 \quad 1 \quad 2 \quad 2.5 \quad 2.9 \quad 3 \quad 4 \]

To move from Q, 2.9 to K, 2.5 you move left on the number line. So the reaction shifts left so the answer is c.

20. (a) no change (b) right (c) left (d) right (e) right (f) no change

21. (a) right, increase (b) no change (c) right, increase (d) no change (e) right, decrease

22. (a) \frac{1}{4} \ (\text{reciprocal when equation is reversed}) \ (b) 16 \ (4 \text{ squared not 2 times 4})

(Note whatever you do the coefficients becomes a power)

23. Answer is d: reverse the equation makes it the reciprocal, and doubling the coefficients causes it to be squared.

24. R \quad \text{CO} \ + \ \text{H}_2\text{O} \rightarrow \text{CO}_2 \ + \ \text{H}_2
We need to rearrange in the form : \( ax^2 + bx + c = 0 \)

So: \( 1.56 (x^2 - 3x +2) = x^2 \)

\[
0.56 x^2 -4.68 x +3.12 = 0
\]

\[
a = 0.56, \quad b = -4.68, \quad \text{and} \quad c = 3.12
\]

\[
x = -b + or - (b^2-4ac)^{1/2} / 2a \quad \text{½ power means square root}
\]

\[
x = 4.86 + or - [(-4.68)^2 -4(0.56)(3.12)] / 2(0.56)
\]

\[
x = 7.6 \text{ M or } .73 \text{ M} \quad \text{depending on whether you add or subtract.}
\]

Note that only one make sense. If you tried to subtract 7.6 in the RICE chart you would get a negative value which is not possible.

So the answer is 0.73 M for CO.