3. Nitramide, $N_2H_2O_2$, decomposes slowly in aqueous solution. This decomposition is believed to occur according to the reaction mechanism below.

Step 1) $N_2H_2O_2 \rightarrow N_2HO_2^- + H^+$ (fast equilibrium)

Step 2) $N_2HO_2^- \rightarrow N_2O + OH^-$ ★RDS (slow) rate = $k[N_2HO_2^-]$

Step 3) $H^+ + OH^- \rightarrow H_2O$ (fast)

Write the rate law for the decomposition of nitramide that is consistent with this mechanism.

rate = $k[N_2H_2O_2]$

4. The reaction A + B → C + D, obeys the rate law expression Rate = k[A][B]. Which of the following proposed mechanisms below that are consistent with this information? Justify your answer.

✓ I. A + B → C + D — one step] rate = $k[A][B]$

✓ II. A + B ↔ E — fast, equilibrium
E → C + D — slow ★RDS] rate = $k[A][B]$ } Because E is an intermediate, use fast equil step to replace [E] w/ $K_{eq}[A][B]$ in rate law!

III. A + B ↔ E — fast, equilibrium
A + E → C + B — slow ★RDS] rate = $k[A]^2[B]$

Both I and II are consistent - they both sum to the overall rxn, and the stoichiometry for both supports the provided rate law (i.e. Stoichiometric coefficient of 1 for both A and B, and they're both 1st order in the given rate law).

5. The rate law for $CO + NO_2 \rightarrow CO_2 + NO$ is rate = $k[NO_2]^2$. Which of the following mechanisms is consistent with the data? Justify your choice.

~~(a)~~ $CO + NO_2 \rightarrow CO_2 + NO$

~~(b)~~ $2\,NO_2 \rightarrow N_2O_4$ fast
$N_2O_4 + 2\,CO \rightarrow 2\,CO_2 + 2\,NO$ slow

(c) $2\,NO_2 \rightarrow NO_3 + NO$ slow
$NO_3 + CO \rightarrow NO_2 + CO_2$ fast

~~(d)~~ $2\,NO_2 \rightarrow 2\,NO + O_2$ slow
$2\,CO + O_2 \rightarrow 2\,CO_2$ fast

1
$2NO_2 \rightarrow NO_3 + NO$
$NO_3 + CO \rightarrow NO_2 + CO_2$ +
$NO_2 + CO \rightarrow CO_2 + NO$

(c) is consistent w/ the data, because the steps sum to the overall rxn, and step 1 is slow and thus the rate-determining step. NO_2 has a stoichiometric coefficient of 2 in that step, and NO_2 is second order in the provided rate law.

Released AP Free Response Practice – Whee!

1. The following results were obtained when the following reaction was studied at 25°C: $2A + B \rightarrow C + D$

Experiment	Initial [A]	Initial [B]	Initial Rate of Formation of C (mol L^{-1} min^{-1})
1	0.25	0.75	4.3×10^{-4}
2	0.75 (3x)	0.75	1.3×10^{-3} (3x)
3	1.50 (2x)	1.50	5.3×10^{-3} (4x)

a. Determine the order of the reaction with respect to A and to B. Justify your answer.

trials 1+2: 3x [A], [B] constant, rate increased by a factor of 3, so the rxn is 1st order w/ respect to A.

trials 2+3: 2x [A] AND 2x [B], rate increased by a factor of 4; since 2x [A] causes 2x rate, 2x [B] must double rate ⇒ 1st order w/ respect to B

b. Write the rate law for the reaction. rate = $k[A][B]$

c. Calculate the value of the rate constant, *k*, for the reaction, specifying units.

$$k = \frac{\text{rate}}{[A][B]} = \frac{4.3E\ M/min}{(0.25\ M)(0.75\ M)} = 0.0023\ M^{-1}\ min^{-1}$$

d. Predict the initial rate of the disappearance of A if $[A]_{init}$ = 0.75 mol L^{-1} and $[B]_{init}$ = 1.50 mol L^{-1}.

rate (of rxn) = $k[A][B] = (0.0023\ M^{-1}\ min^{-1})(0.75\ M)(1.50\ M) = 0.0026\ M/min$

⇒ rate of A consumption = 2 (stoich. coeff.) × rate of rxn = $2\left(0.0026 \frac{M}{min}\right) = 0.0052 \frac{M}{min}$

e. Is the reaction mechanism represented below consistent with the rate law developed in part (b)? Justify your answer.

$B \leftrightarrow M$	Fast equilibrium
$M + A \rightarrow C + X$	Slow
$X + A \rightarrow D$	Fast
$2A + B \rightarrow C + D$	

b/c the stoich. coeff. of M and A are 1

Yes, this rxn mechanism is consistent w/ the rate law from part b. The mechanism steps sum to the overall rxn. Also, the rate-determing (slow) step has a rate law = $k[M][A]$, but since M is an intermediate, we can use the fast equilibrium step to replace $[M] = K_{eq}[B]$, so the rate law predicted by this mechanism = $k(K_{eq}[B])[A] = k[B][A]$.