HL Answers to questions on Reaction mechanisms

1. i. If the second step is the slowest step the overall rate will equal the rate for that step. The rate for the second step is proportional to $[H_2(g)]$ and $[N_2O_2(g)]$, i.e.

rate $\propto [H_2(g)] \times [N_2O_2(g)]$ or rate = $k[H_2(g)][N_2O_2(g)]$ where k is the rate constant.

However $N_2O_2(g)$ is an intermediate and its formation depends on the first step, i.e. $[NO(g)]^2$.

Hence rate = $k[H_2(g)]\,[NO(g)]^2$ which is the same as the experimentally determined rate equation.

ii. (i) rate = $k[NO(g)]^2$

(ii) rate = $k[H_2(g)]^2[NO(g)]^2$

2. Step 1: $2NO_2(g) \rightarrow NO_3 + NO$ (slow step)

Step 2: $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$ (fast step)

An equally plausible alternative mechanism could be:

Step 1: $2NO_2(g) \rightarrow N_2O_4$ (slow step)

Step 2: $N_2O_4(g) + CO(g) \rightarrow NO(g) + NO_2(g) + CO_2(g)$ (fast step)

(Note that both proposed mechanisms are consistent with the rate equation and both give the same overall equation for the reaction.)

3. i. $2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$

Ii. First order with respect to chlorine gas, third order overall (since it is second order with respect to [NO(g)]).

iii. Rate= $k[Cl_2(g)][NO(g)]^2$

4. i. The rate equation is rate = $k[A]^x[B]^y$

From Experiment 1 the numerical value of k without units must be 1 as the rate = 1 mol dm^{-3} s^{-1} and [A] and [B] are both 1 mol dm^{-3}. However the actual value of k cannot be known as although $1^x \times 1^y = 1$ the values of x and y are unknown and the concentration powers will determine the units of k.

ii. From Experiments 1 and 2 doubling [A] and quadrupling [B] is consistent with x=1 and y = 1 as the rate increases eightfold. This is confirmed by Experiments 1 and 3 since tripling [A] and increasing [B] 9 times will increase the rate by 27 times. Comparing Experiments 1 and 4, quadrupling [A] and doubling [B] will increase the rate eightfold so ***z*** = 8.00, i.e. the rate = 8.00 mol dm^{-3} s^{-1}.

iii. Rate = $k[A]^x[B]^y$ and x = 1 and y = 1.
From Experiment 1, rate = 1.00 mol dm^{-3} s^{-1} = k x 1.00 mol dm^{-3} x 1.00 mol dm^{-3}
So k = 1.00 mol^{-1} dm^3 s^{-1}

iv. The reaction is first order with respect to both [A] and [B] and is second order overall.

Possible mechanism:

Step 1: A(g) + B(g) → A—B(g) (slow step)

Step 2: A—B(g) + B(g) → products (fast step)

Alternative possible mechanism:

Step 1: B(g) + B(g) → B—B(g) (slow step)

Step 2: B—B(g) + A(g) → products (fast step)

v. From Experiments 1 and 2 doubling [A] and quadrupling [B] is consistent with x = 3 and y = 0 as the rate increases eightfold. This is confirmed by Experiments 1 and 3 since increasing [B] 9 times will have no effect on the rate whereas tripling [A] will increase the rate 27 times. Comparing Experiments 1 and 4, doubling [B] will not affect the rate but quadrupling [A] will increase the rate 64 times so ***z*** = 64.00,i.e. the rate = 64.00 mol dm^{-3} s^{-1}.

vi. Rate = $k[A]^x[B]^y$ and x = 3 and y = 0.
From Experiment 1, rate = 1.00 mol dm^{-3} s^{-1} = k x $(1.00 \text{ mol } dm^{-3})^3$
So k = 1.00 mol^{-2} dm^6 s^{-1}

vii. The reaction is third order with respect to [A] and zero order with respect to [B] and is third order overall.

Possible mechanism:

Step 1: $A(g) + A(g) \rightarrow A_2(g)$ (fast step)

Step 2: $A_2(g) + A(g) \rightarrow A_3(g)$ (slow step)

Step 3: $A_3(g) + B(g) \rightarrow A—B(g) + A_2(g)$ (fast step)

Step 4: A—B(g) + B(g) →products (fast step)

viii. A mechanism must be consistent with the rate equation but the rate equation does not prove that a mechanism is correct. Both of the proposed mechanisms are consistent with the possible rate equations derived from the experimental data. The mechanism proposed for the second order reaction is the simplest and by Occam's razor seems much the most likely but the mechanism proposed for the third order reaction cannot be definitely ruled out. More experimental data is needed to determine which is the correct rate equation.