1.   (a)   **Between experiments (1) and (2), [NO] is constant. Doubling $[O_2]$ leads to the initial reaction rate doubling:**

the reaction is first order with respect to O_2.

Between experiments (1) and (3), $[O_2]$ is constant. Doubling [NO] leads to the initial reaction rate increases by a factor of four:

the reaction is second order with respect to NO.

Thus,

$$\text{rate } \alpha \ [O_2][NO]^2 = k[O_2][NO]^2$$

Using experiment (1), rate = 3.20×10^{-3} mol L^{-1} s^{-1} when $[O_2] = 1.10 \times 10^{-2}$ mol L^{-1} and [NO] = 1.30×10^{-2} mol L^{-1}. Hence, for k and its units:

$$3.20 \times 10^{-3} \text{ mol } L^{-1} = k \times (1.10 \times 10^{-2} \text{ mol } L^1) \times (1.30 \times 10^{-2} \text{ mol } L^1)^2$$

$$(\text{mol } L^{-1} \text{ s}^{-1}) = (\text{units of } k) \times (\text{mol } L^{-1}) \times (\text{mol } L^{-1})^2$$

$$k = 1.7 \times 10^3 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$$

(b)   **According to the reaction equation:**

$$O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$$

Two moles of NO_2 are produced for every mole of O_2 which reacts. The react of formation of NO_2 is thus twice the rate of consumption of oxygen. If the initial rate of consumption of oxygen is 1×10^3 mol L^{-1} s^{-1}, the initial rate of formation of $NO_2(g)$ is 2×10^3 mol L^{-1} s^{-1}.

2.   **For a first order reaction, the rate constant and half life are related by $k = \dfrac{\ln 2}{t_{1/2}}$.**

Thus,

$$k = \frac{\ln 2}{(6.00 \times 10^4 \text{ s})} = 1.16 \times 10^{-5} \text{ s}^{-1}$$

3.   **The rate constants at two different temperatures are related through the Arrhenius equation:**

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Thus,

$$\ln\left(\frac{0.248\,\text{L}\,\text{mol}^{-1}\,\text{s}^{-1}}{0.208\,\text{L}\,\text{mol}^{-1}\,\text{s}^{-1}}\right) = \frac{E_\text{a}}{(8.314\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})}\left(\frac{1}{(37+273)\text{K}} - \frac{1}{(40+273)\text{K}}\right)$$

$E_\text{a} = 47300\ \text{J mol}^{-1} = 47.3\ \text{kJ mol}^{-1}$

The "A" factor can be determined using k and E_a at either temperature using the Arrhenius equation:

$$k = A\,e^{-E_\text{a}/RT}$$

At T = 37 °C, k = 0.208 mol^{-1} L s^{-1},

$$0.208\ \text{mol L}^{-1}\ \text{s}^{-1} = A \times (e^{-47300/(8.314\times(37+273))}$$

$A = 1.94 \times 10^7\ \text{mol}^{-1}\ \text{L s}^{-1}$ (note that "A" has the same units as k)

4.   (a)   As the second reaction is slow, it is rate determining. From the mechanism, the rate of this step is given by:

rate $= k_2[\text{O}_3][\text{O}]$

As O is a highly reactive intermediate, its concentration cannot be included in the rate equation which is to be experimental tested. As the first step is fast, the equilibrium between O_3 and O_2 + O will be set up rapidly and maintained for most of the reaction. For an equilibrium,

rate forward reaction = rate backward reaction

$$k_1[\text{O}_3] = k_{-1}[\text{O}_2][\text{O}] \text{ or } [\text{O}] = \frac{k_1}{k_{-1}}\frac{[\text{O}_3]}{[\text{O}_2]}$$

Hence,

rate $= k_2[\text{O}_3][\text{O}]$

$$= k_2[\text{O}_3] \times \frac{k_1}{k_{-1}}\frac{[\text{O}_3]}{[\text{O}_2]} = \frac{k_1 k_2}{k_{-1}}\frac{[\text{O}_3]^2}{[\text{O}_2]} = k\frac{[\text{O}_3]^2}{[\text{O}_2]} \text{ where } k = \frac{k_1 k_2}{k_{-1}}$$

(b)   The rate determining step (step 2) involves the reaction of one molecule of O_2 with one atom of O. The molecularity is thus two: a bimolecular reaction.