Questions

1 Bromine and nitrogen(II) oxide react according to the following equation.

$Br_2(g) + 2NO(g) \rightarrow 2NOBr(g)$

Which rate equation is consistent with the experimental data?

$[Br_2]$/ mol dm^{-3}	[NO]/ mol dm^{-3}	Rate/ mol dm^{-3} s^{-1}
0.10	0.10	1.0×10^{-6}
0.20	0.10	4.0×10^{-6}
0.20	0.40	4.0×10^{-6}

A. rate = $k[Br_2]^2[NO]$

B. rate = $k[Br_2][NO]^2$

C. rate = $k[Br_2]^2$

D. rate = $k[NO]^2$ [1]

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2 The rate information below was obtained for the following reaction at a constant temperature.

$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$

$[NO_2]$/ mol dm^{-3}	$[F_2]$/ mol dm^{-3}	Rate/ mol dm^{-3} s^{-1}
2.0×10^{-3}	1.0×10^{-2}	4.0×10^{-4}
4.0×10^{-3}	1.0×10^{-2}	8.0×10^{-4}
4.0×10^{-3}	2.0×10^{-2}	1.6×10^{-3}

What are the orders of the reaction with respect to NO_2 and F_2?

A. NO_2 is first order and F_2 is second order.

B. NO_2 is second order and F_2 is first order.

C. NO_2 is first order and F_2 is first order.

D. NO_2 is second order and F_2 is second order. [1]

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3 Which step is the rate-determining step of a reaction?

A. The step with the lowest activation energy.

B. The final step.

C. The step with the highest activation energy.

D. The first step. [1]

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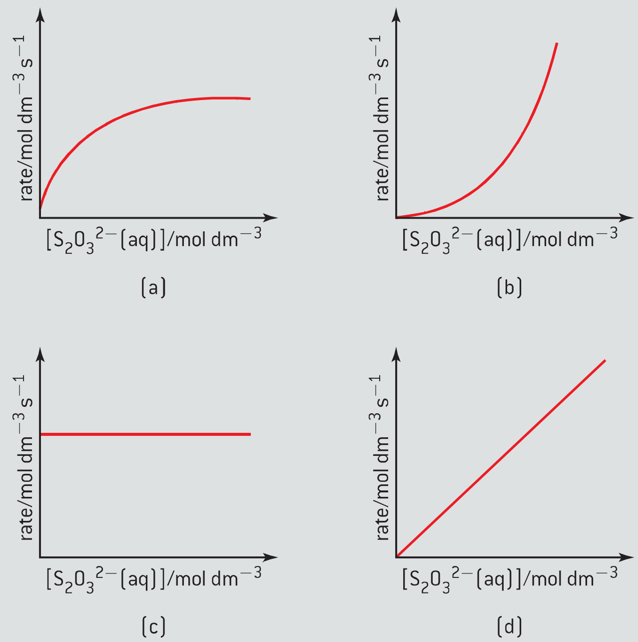
4 A student experimentally determined the rate expression to be:

rate = $k[S_2O_3^{2-}(aq)]^2$

Which graph is consistent with this information? [1]



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5 Consider the following reaction:

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

At $T < 227$ °C the rate expression is rate = $k[NO_2]^2$. Which of the following mechanisms is consistent with this rate expression?

A. $NO_2 + NO_2 \rightleftharpoons N_2O_4$ *fast*
$N_2O_4 + 2CO \rightarrow 2NO + 2CO_2$ *slow*

B. $NO_2 + CO \rightarrow NO + CO_2$ *slow*

C. $NO_2 \rightarrow NO + O$ *slow*
$CO + O \rightarrow CO_2$ *fast*

D. $NO_2 + NO_2 \rightarrow NO_3 + NO$ *slow*
$NO_3 + CO \rightarrow NO_2 + CO_2$ *fast* [1]

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6 Consider the following reaction.

$$2Q(g) + R(g) \rightarrow X(g) + Y(g)$$

This reaction occurs according to the following mechanism:

$Q(g) + R(g) \rightarrow X(g) + M(g)$ *slow*

$M(g) + Q(g) \rightarrow Y(g)$ *fast*

Which of the following is correct?

I. M(g) is a reaction intermediate.

II. Rate $= k[Q][R]$

III. The slow-step is the rate-determining step.

A. I and II only

B. I and III only

C. II and III only

D. I, II, and III

7 Hydrogen gas, $H_2(g)$, reacts with iodine gas, $I_2(g)$, to form hydrogen iodide, HI(g):

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

The mechanism of the two-step reaction is considered to be:

step 1: $I_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2I(g)$ *fast*

step 2: $2I(g) + H_2(g) \xrightarrow{k_2} 2HI(g)$ *slow*

What is the rate equation for the overall reaction?

A. rate $= k[H_2][I]^2$

B. rate $= k[H_2]$

C. rate $= k[I_2]$

D. rate $= k[H_2][I_2]$

8 What are the units of the frequency factor in the Arrhenius equation?

A. kJ mol^{-1}

B. J mol^{-1}

C. s^{-1}

D. Depends on the units of k.

9 Ozone is considered to decompose according to the following two-step mechanism:

step 1: $O_3(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2(g) + O(g)$ *fast*

step 2: $O(g) + O_3(g) \xrightarrow{k_2} 2O_2(g)$ *slow*

Which of the following are correct?

I. The overall reaction is $2O_3(g) \rightarrow 3O_2(g)$.

II. O(g) is a reaction intermediate.

III. The rate equation is:
rate $= k[O_3]^2[O_2]^3$

A. I and II only

B. I and III only

C. II and III only

D. I, II, and III

10 Consider the following reaction:

$$A(g) + B(g) \rightarrow C(g) + D(g)$$

and the following experimental initial rate data:

	[A(g)]/ mol dm^{-3}	[B(g)]/ mol dm^{-3}	Initial rate/ mol $dm^{-3}s^{-1}$
Experiment 1	1.50×10^{-2}	1.50×10^{-2}	2.32×10^{-3}
Experiment 2	1.50×10^{-2}	3.00×10^{-2}	4.64×10^{-3}
Experiment 3	3.00×10^{-2}	1.50×10^{-2}	4.64×10^{-3}

a) Deduce the orders with respect to each reactant and the overall reaction order.

b) Deduce the rate equation.

c) Calculate the value of the rate constant, k, for the reaction from experiment 2 and state its units.

d) Determine the rate of the reaction when $[A(g)] = 2.00 \times 10^{-2}$ mol dm^{-3} and $[B(g)] = 4.00 \times 10^{-2}$ mol dm^{-3}

11 The rate constant, k_1, of a first-order reaction is 6.30×10^3 s^{-1} at 32 °C and the corresponding rate constant, k_2, is 2.25×10^5 s^{-1} at 83 °C.

a) Deduce the activation energy, E_a, in kJ mol^{-1}, correct to **two** significant figures.

b) Calculate the rate constant, k_3, in s^{-1}, at 20 °C.

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End of topic questions (page 387)

1. C; in order to solve this question we can use the working method to deduce the rate equation from the method of initial rates:

$$\frac{rate\ 1}{rate\ 2} = \frac{(0.10)^x}{(0.20)^x}\frac{(0.10)^y}{(0.10)^y} = \frac{1.0 \times 10^{-6}}{4.0 \times 10^{-6}} = (0.5)^x = 0.25, \text{ so } x = 2;$$

$$\frac{rate\ 2}{rate\ 3} = \frac{(0.20)^x}{(0.20)^x}\frac{(0.10)^y}{(0.40)^y} = \frac{4.0 \times 10^{-6}}{4.0 \times 10^{-6}} = (0.25)^y = 1, \text{ so } y = 0;$$

the reaction is second order with respect to Br_2:

$rate = k[Br_2]^2$

2. C;

$$\frac{rate\ 1}{rate\ 2} = \frac{(0.002)^x}{(0.004)^x}\frac{(0.01)^y}{(0.01)^y} = \frac{4.0 \times 10^{-4}}{8.0 \times 10^{-4}} = (0.5)^x = 0.50, \text{ so } x = 1;$$

$$\frac{rate\ 2}{rate\ 3} = \frac{(0.004)^x}{(0.004)^x}\frac{(0.01)^y}{(0.02)^y} = \frac{8.0 \times 10^{-4}}{1.6 \times 10^{-3}} = (0.50)^y = 0.5, \text{ so } y = 1;$$

the reaction is first order with respect to NO_2 and F_2;

3. C; reactions may occur by more than one step and the slow step determines the rate of the reaction; the slow step is termed the rate-determining step (RDS); this is the step with the highest activation energy;

4. B; in a a rate–concentration plot for a second order reaction (figure (b)), the rate is directly proportional to the square of the concentration, because rate $= k[A]^2$ for a second order reaction;

5. D;

step 1	$NO_2 + NO_2 \rightleftharpoons \cancel{N_2O_4}$	*fast*
step 2	$\cancel{N_2O_4} + 2CO \rightarrow 2NO + 2CO_2$	*slow*
overall	$2NO_2 + 2CO \rightarrow 2NO + 2CO_2$	

this mechanism does not result in the reaction in question;

$NO_2 + CO \rightarrow NO + CO_2$	*slow*

this mechanism with one RDS, the rate expression is rate $= k[NO_2][CO]$;

step 1	$NO_2 \rightarrow NO + \cancel{O}$	*slow*
step 2	$CO + \cancel{O} \rightarrow CO_2$	*fast*
overall	$NO_2 + CO \rightarrow NO + CO_2$	

this mechanism does produce the correct overall equation but not the correct rate expression;

step 1	$\cancel{NO_2} + NO_2 \rightarrow \cancel{NO_3} + NO$	*slow*
step 2	$\cancel{NO_3} + CO \rightarrow \cancel{NO_2} + CO_2$	*fast*
overall	$NO_2 + CO \rightarrow NO + CO_2$	

this mechanism does produce the correct overall equation and the correct rate expression;

6. D;

step 1	$Q(g) + R(g) \rightarrow X(g) + \cancel{M(g)}$	*slow*
step 2	$\cancel{M(g)} + Q(g) \rightarrow Y(g)$	*fast*
overall	$2Q(g) + R(g) \rightarrow X(g) + Y(g)$	

rate $= k[Q][R]$;

an analysis of the working above determines that all three statements are valid;

7. D; the iodine atom is a reaction intermediate; be careful that this does not mask the fact that iIodine (I) is important in the understanding of this mechanism; as a reaction intermediate, it is formed in the initial *fast* step and is consumed in the subsequent *slow* step; however, its formation and presence in the slow step is dependent on its formation from the iodine molecule (I_2) in the first fast step and for this reason the iodine molecule must be included in the rate expression; the other species in the rate expression will be the hydrogen molecule, hence the rate expression is rate $= k[I_2][H_2]$;

8. D; the frequency factor is essentially the number of times reactants will approach the activation energy barrier in unit time; the units of the frequency factor (A) are identical to those of the rate constant (k) and will vary depending on the order of the reaction; if the reaction is a first order reaction, the units will be s^{-1}; this is why answer C may be chosen by mistake;

9. A;

step 1	$O_3(g) \rightleftharpoons O_2(g) + \Theta(g)$	*fast*
step 2	$\Theta(g) + O_3(g) \rightarrow 2O_2(g)$	*slow*
overall	$2O_3(g) \rightleftharpoons 3O_2(g)$	

In this mechanism, the reaction intermediate if the oxygen atom (O) as it is produced and the consumed in a subsequent step; as its presence in the slow step is dependent on the fast step, the reactant of the fast step must be included in the rate expression; therefore, the rate expression for this mechanism is rate $= k[O_3]^2$ and not as stated in statement III;

10. a) $$\frac{rate\ 1}{rate\ 2} = \frac{(0.0150)^a}{(0.0150)^a}\frac{(0.0150)^b}{(0.0300)^b} = \frac{2.32 \times 10^{-3}}{4.64 \times 10^{-3}} = (0.500)^b = 0.50, \text{ so } b = 1$$

$$\frac{rate\ 1}{rate\ 3} = \frac{(0.0150)^a}{(0.0300)^a}\frac{(0.0150)^b}{(0.0150)^b} = \frac{2.32 \times 10^{-3}}{4.64 \times 10^{-3}} = (0.500)^a = 0.5, \text{ so } a = 1$$

the reaction is first order with respect to A and B; the overall reaction order is second order;

b) rate $= k[A][B]$

c) $$k = \frac{\text{rate}}{[A][B]}$$

$$K = \frac{4.64 \times 10^{-3}\ mol\ dm^{-3}s^{-1}}{1.50 \times 10^{-2}\ mol\ dm^{-3} \times 3.00 \times 10^{-2}\ mol\ dm^{-3}} = 1.03 \times 10^{1}\ mol^{-1}dm^{3}s^{-1}$$

d) rate $= k[A][B]$

$= (1.03 \times 10^{1}\ mol^{-1}\ dm^{3}s^{-1}) \times (2.00 \times 10^{-2}\ mol\ dm^{-3} \times (4.00 \times 10^{-2}\ mol\ dm^{-3})$

$= 8.25 \times 10^{-3}\ mol\ dm^{-3}s^{-1}$

11. a) $$E_a = \frac{ln\frac{6.30 \times 10^{3}}{2.25 \times 10^{5}} \times 8.31}{\frac{1}{356} - \frac{1}{305}} = \frac{-29.7}{-4.70 \times 10^{-4}} = 6.33 \times 10^{4}\ J\ mol^{-1}$$

b) $$6.33 \times 10^{4} = \frac{ln\frac{k_3}{6.30 \times 10^{3}} \times 8.31}{\frac{1}{305} - \frac{1}{293}}$$

In the above expression, use the value of k_2 and the temperature for k_1; the combination should be either k_1 and T_1, or k_2 and T_2;

$$\ln\frac{k_3}{6.30 \times 10^{3}} = -1.02286$$

$\ln k_3 = -1.02286 + \ln(6.30 \times 10^{3}) = 7.72544$

$k_3 = 2.27 \times 10^{3}\ s^{-1}$

There is an alternative method; retain a large number of significant figures in the intermediate values:

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$ln_A = lnk_1 + \frac{E_a}{RT_1} = \ln(6.30 \times 10^3) + \frac{63300}{8.31 \times 305} = 33.7231$$

$$lnk_3 = ln_A - \frac{E_a}{RT_3} = 33.7231 - \frac{63300}{8.31 \times 293} = 7.7254$$

$$k_3 = 2.27 \times 10^3 \text{ s}^{-1}$$