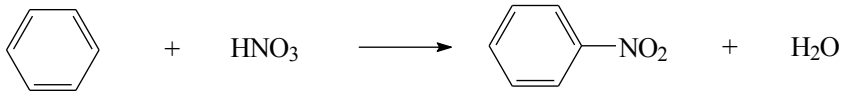
Marks 5

- The nitration of benzene to form nitrobenzene may be written with the following stoichiometry.



The reaction was performed in the presence of excess concentrated sulfuric acid and the following data were obtained.

Experiment number	initial [benzene] (M)	initial [nitric acid] (M)	[nitrobenzene] (M) after 100 s
1	0.010	1.0	1.2×10^{-4}
2	0.020	1.0	2.4×10^{-4}
3	0.020	0.50	1.2×10^{-4}

Determine the rate of the reaction for Experiment 1.

Answer:

What is the rate equation for this reaction?

Rate =

What is the value of the rate constant?

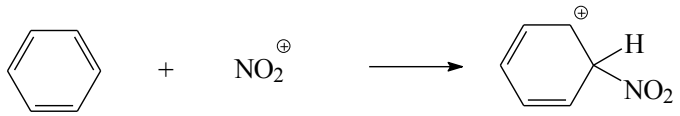
k =

THIS QUESTION CONTINUES ON THE NEXT PAGE

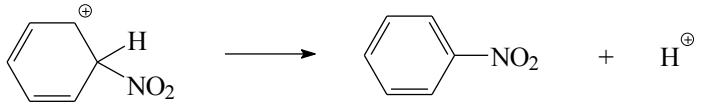
Marks
2

Show that the observed kinetics [in 2004-N-11] are consistent with the following mechanism.

$$HNO_3 + H_2SO_4 \rightleftharpoons NO_2^+ + HSO_4^- + H_2O \qquad \text{(fast)}$$



(slow)



(fast)

Marks 5

- Consider the following reaction.

$$2ClO_2(aq) + 2OH^-(aq) \rightarrow ClO_3^-(aq) + ClO_2^-(aq) + H_2O(l)$$

A series of experiments gave the rate data shown in the table below.

Experiment number	initial $[ClO_2]$ (M)	initial $[OH^-]$ (M)	initial rate of decrease of $[ClO_2]$ ($M\ s^{-1}$)
1	0.0500	0.100	5.75×10^{-2}
2	0.100	0.100	2.30×10^{-1}
3	0.100	0.050	1.15×10^{-1}

Determine the rate expression for the above reaction.

Rate =

What is the value of the rate constant? Include units in your answer.

k =

What is the relationship between the rate of decrease of $[ClO_2]$ and the rate of increase of $[ClO_3^-]$?

Marks 2

- It has been proposed that the reaction $Cl_2(g) + CHCl_3(g) \rightarrow HCl(g) + CCl_4(g)$ proceeds by the following mechanism:

$$Cl_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Cl(g) \qquad \text{(fast equilibrium)}$$

$$Cl(g) + CHCl_3(g) \xrightarrow{k_2} HCl(g) + CCl_3(g) \qquad \text{(slow)}$$

$$CCl_3(g) + Cl(g) \xrightarrow{k_3} CCl_4(g) \qquad \text{(fast)}$$

Derive the rate expression for this mechanism.

Answer:

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks 5

- The major pollutants NO(g), CO(g), NO_2(g) and CO_2(g), which are emitted by cars, can react according to the following equation.

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

The following rate data were collected at 225 ^oC.

Experiment	$[NO_2]_0$ (M)	$[CO]_0$ (M)	Initial rate ($d[NO_2]/dt$, M s^{-1})
1	0.263	0.826	1.44×10^{-5}
2	0.263	0.413	1.44×10^{-5}
3	0.526	0.413	5.76×10^{-5}

Determine the rate law for the reaction.

Calculate the value of the rate constant at 225 ^oC.

	Answer:

Calculate the rate of appearance of CO_2 when $[NO_2] = [CO] = 0.500$ M.

Answer:

Suggest a possible mechanism for the reaction based on the form of the rate law. Explain your answer.

Marks 5

- Phosgene is a toxic gas prepared by the reaction of carbon monoxide with chlorine:

$$CO(g) + Cl_2(g) \rightarrow COCl_2(g)$$

The following data were obtained in a kinetics study of its formation at 150 °C.

Experiment	initial [CO] (M)	initial [Cl_2] (M)	Initial rate ($M\ s^{-1}$)
1	1.00	0.100	1.29×10^{-29}
2	0.100	0.100	1.33×10^{-30}
3	0.100	1.00	1.30×10^{-29}
4	0.100	0.0100	1.32×10^{-31}

Determine the rate law for the reaction.

Calculate the value of the rate constant at 150 ^{o}C.

Answer:

Calculate the rate of appearance of phosgene when [CO] = [Cl_2] = 1.3 M.

Answer:

	Marks
• Draw the potential energy diagram for an endothermic reaction. Indicate on the diagram the activation energy for both the forward and reverse reaction, and the enthalpy of reaction.	**4**
Would you expect the forward or the reverse reaction to be faster? Why?	

Marks

- Consider the reaction: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

  The experimentally determined rate equation is: Rate = $k[NO_2(g)]^2$

  Show the rate expression is consistent with the following mechanism:

  4

Step 1	$2NO_2(g) \rightleftharpoons N_2O_4(g)$	fast
Step 2	$N_2O_4(g) \rightarrow NO(g) + NO_3(g)$	slow
Step 3	$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$	fast

- The rate constant of a particular reaction quadruples when the temperature is increased from 30 °C to 50 °C. Calculate the activation energy, E_a, for this reaction.

  2

E_a =

• Briefly describe collision theory and how it relates to the Arrhenius equation.	**Marks 3**

Marks 4

- The following data were obtained for the reaction of iodine atoms in the gas phase in the presence of argon.

$$2I(g) + Ar(g) \rightarrow I_2(g) + Ar(g)$$

Experiment Number	Initial [I] (M)	Initial [Ar] (M)	Initial Reaction Rate $-d[I(g)]/dt$ ($M\ s^{-1}$)
1	1.0×10^{-5}	1.0×10^{-3}	8.70×10^{-4}
2	2.0×10^{-5}	1.0×10^{-3}	3.48×10^{-3}
3	2.0×10^{-5}	5.0×10^{-3}	1.74×10^{-2}

Derive an expression for the rate law for the formation of $I_2(g)$ and calculate the value of the rate constant for this reaction.

Rate law:

Rate constant:

Calculate the rate of appearance of $I_2(g)$ when $[I(g)] = 1.0 \times 10^{-3}$ M and $[Ar(g)] = 1.0 \times 10^{-2}$ M.

Answer: