AP Questions: Kinetics

1972

$$2\ A + 2\ B \rightarrow C + D$$

The following data about the reaction above were obtained from three experiments:

Experiment	[A]	[B]	Initial Rate of Formation of C (mole·liter^{-1}min^{-1})
1	0.60	0.15	6.3×10^{-3}
2	0.20	0.60	2.8×10^{-3}
3	0.20	0.15	7.0×10^{-4}

(a) What is the rate equation for the reaction?

(b) What is the numerical value of the rate constant k? What are its dimensions?

(c) Propose a reaction mechanism for this reaction.

1976 D

Changing the temperature and no other conditions changes the rates of most chemical reactions. Two factors are commonly cited as accounting for the increased rate of chemical reaction as the temperature is increased. State briefly and discuss the two factors. Which of the two is more important?

1977 B

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

For the reaction above, the rate constant at 380°C for the forward reaction is 2.6×10^3 liter^2/mole^2-sec and this reaction is first order in O_2 and second order in NO. The rate constant for the reverse reaction at 380°C is 4.1 liter/mole-sec and this reaction is second order in NO_2.

(a) Write the equilibrium expression for the reaction as indicated by the equation above and calculate the numerical value for the equilibrium constant at 380°C.

(b) What is the rate of the production of NO_2 at 380°C if the concentration of NO is 0.0060 mole/liter and the concentration of O_2 is 0.29 mole/liter?

(c) The system above is studied at another temperature. A 0.20 mole sample of NO_2 is placed in a 5.0 liter container and allowed to come to equilibrium. When equilibrium is reached, 15% of the original NO_2 has decomposed to NO and O_2. Calculate the value for the equilibrium constant at the second temperature.

1981 B

$$A(aq) + 2\ B(aq) \rightarrow 3\ C(aq) + D(aq)$$

For the reaction above, carried out in solution of 30°C, the following kinetic data were obtained:

Experiment	Initial Conc. of Reactants (mole·liter^{-1}) A_o	B_o	Initial Rate of Reaction (mole·liter^{-1}·hr^{-1})
1	0.240	0.480	8.00
2	0.240	0.120	2.00
3	0.360	0.240	9.00
4	0.120	0.120	0.500
5	0.240	0.0600	1.00
6	0.0140	1.35	?

(a) Write the rate-law expression for this reaction.

(b) Calculate the value of the specific rate constant k at 30°C and specify its units.

(c) Calculate the value of the initial rate of this reaction at 30°C for the initial concentrations shown in experiment 6.

(d) Assume that the reaction goes to completion. Under the conditions specified for experiment 2, what would be the final molar concentration of C?

1983 C

Graphical methods are frequently used to analyze data and obtain desired quantities.

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

The following data give the value of the rate constant at various temperatures for the gas phase reaction above.

T (K)	k (litre/mol sec)
647	8.58×10^{-5}
666	2.19×10^{-4}
683	5.11×10^{-4}
700	1.17×10^{-3}
716	2.50×10^{-3}

Describe, without doing any calculations, how a graphical method can be used to obtain the activation energy for this reaction.

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

The following data give the partial pressure of A as a function of time and were obtained at 100°C for the reaction above.

P_A (mm Hg)	t (sec)
348	0
247	600
185	1200
105	2400
58	3600

Describe, without doing any calculations, how graphs can be used to determine whether this reaction is first or second order in A and how these graphs are used to determine the rate constant.

1984 B

For a hypothetical chemical reaction that has the stoichiometry $2\ X + Y \rightarrow Z$, the following initial rate data were obtained. All measurements were made at the same temperature.

Initial Rate of Formation of Z, ($mol \cdot L^{-1} \cdot sec^{-1}$)	Initial $[X]_o$, ($mol \cdot L^{-1}$)	Initial $[Y]_o$, ($mol \cdot L^{-1}$)
7.0×10^{-4}	0.20	0.10
1.4×10^{-3}	0.40	0.20
2.8×10^{-3}	0.40	0.40
4.2×10^{-3}	0.60	0.60

(a) Give the rate law for this reaction from the data above.

(b) Calculate the specific rate constant for this reaction and specify its units.

(c) How long must the reaction proceed to produce a concentration of Z equal to 0.20 molar, if the initial reaction concentrations are $[X]_o = 0.80$ molar, $[Y]_o = 0.60$ molar and $[Z]_0 = 0$ molar?

(d) Select from the mechanisms below the one most consistent with the observed data, and explain your choice. In these mechanisms M and N are reaction intermediates.

(1)	$X + Y \rightarrow M$	(slow)	(2)	$X + X \leftrightarrow M$	(fast)	(3)	$Y \rightarrow M$	(slow)
	$X + M \rightarrow Z$	(fast)		$Y + M \rightarrow Z$	(slow)		$M + X \rightarrow N$	(fast)
							$N + X \rightarrow Z$	(fast)

1985 D

$$PCl_3(g) + Cl_2(g) \leftrightarrow PCl_5(g)$$

In the equation above, the forward reaction is first order in both PCl_3 and Cl_2 and the reverse reaction is first order in PCl_5.

(a) Suppose that 2 moles of PCl_3 and 1 mole of Cl_2 are mixed in a closed container at constant temperature. Draw a graph that shows how the concentrations of PCl_3, Cl_2, and PCl_5 change with time until after equilibrium has been firmly established.

(b) Give the initial rate law for the forward reaction.

(c) Provide a molecular explanation for the dependence of the rate of the forward reaction on the concentrations of the reactants.

(d) Provide a molecular explanation for the dependence of the rate of the forward reaction on temperature.

1986 D

The overall order of a reaction may not be predictable from the stoichiometry of the reaction.

(a) Explain how this statement can be true.

(b) $2\ XY \rightarrow X_2 + Y_2$

1. For the hypothetical reaction above, give a rate law that shows that the reaction is first order in the reactant XY.
2. Give the units for the specific rate constant for this rate law.
3. Propose a mechanism that is consistent with both the rate law and the stoichiometry.

1987 B

$$2\ HgCl_2(aq) + C_2O_4^{2-} \rightarrow 2\ Cl^- + 2\ CO_2(g) + Hg_2Cl_2(aq)$$

The equation for the reaction between mercuric chloride and oxalate ion in hot aqueous solution is shown above. The reaction rate may be determined by measuring the initial rate of formation of chloride ion, at constant temperature, for various initial concentrations of mercuric chloride and oxalate as shown in the following table

Experi-ment	Initial $[HgCl_2]$	Initial $[C_2O_4^{2-}]$	Initial Rate of For-mation of Cl^- ($mol{\cdot}L^{-1}{\cdot}min^{-1}$)
(1)	0.0836 M	0.202M	0.52×10^{-4}
(2)	0.0836 M	0.404M	2.08×10^{-4}
(3)	0.0418 M	0.404M	1.06×10^{-4}
(4)	0.0316 M	?	1.27×10^{-4}

(a) According to the data shown, what is the rate law for the reaction above?

(b) On the basis of the rate law determined in part (a), calculate the specific rate constant. Specify the units.

(c) What is the numerical value for the initial rate of disappearance of $C_2O_4^{2-}$ for Experiment 1?

(d) Calculate the initial oxalate ion concentration for Experiment 4.

1989 D

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g) \quad \Delta H^\circ = -137\text{ kJ}$$

Account for the following observations regarding the exothermic reaction represented by the equation above.

(a) An increase in the pressure of the reactants causes an increase in the reaction rate.

(b) A small increase in temperature causes a large increase in the reaction rate.

(c) The presence of metallic nickel causes an increase in reaction rate.

(d) The presence of powdered nickel causes a larger increase in reaction rate than does the presence of a single piece of nickel of the same mass.

1990 D

Consider the following general equation for a chemical reaction.

$$A(g) + B(g) \rightarrow C(g) + D(g) \qquad \Delta H^\circ\text{ reaction} = -10\text{ kJ}$$

(a) Describe the two factors that determine whether a collision between molecules of A and B results in a reaction.

(b) How would a decrease in temperature affect the rate of the reaction shown above? Explain your answer.

(c) Write the rate law expression that would result if the reaction proceeded by the mechanism shown below.

$A + B \leftrightarrow [AB]$ (fast)

$[AB] + B \rightarrow C + D$ (slow)

(d) Explain why a catalyst increases the rate of a reaction but does not change the value of the equilibrium constant for that reaction.

1991 B

$$2\ ClO_2(g) + F_2(g) \rightarrow 2\ ClO_2F(g)$$

The following results were obtained when the reaction represented above was studied at 25°C.

Experiment	Initial $[ClO_2]$, $(mol\cdot L^{-1})$	Initial $[F_2]$, $(mol\cdot L^{-1})$	Initial Rate of Increase of $[ClO_2F]$, $(mol\cdot L^{-1}\cdot sec^{-1})$
1	0.010	0.10	2.4×10^{-3}
2	0.010	0.40	9.6×10^{-3}
3	0.020	0.20	9.6×10^{-3}

(a) Write the rate law expression for the reaction above.

(b) Calculate the numerical value of the rate constant and specify the units.

(c) In experiment 2, what is the initial rate of decrease of $[F_2]$?

(d) Which of the following reaction mechanisms is consistent with the rate law developed in (a). Justify your choice.

I.
$ClO_2 + F_2 \leftrightarrow ClO_2F_2$ (fast)
$ClO_2F_2 \rightarrow ClO_2F + F$ (slow)
$ClO_2 + F \rightarrow ClO_2F$ (fast)

II.
$F_2 \rightarrow 2\ F$ (slow)
$2\ (ClO_2 + F \rightarrow ClO_2F)$ (fast)

1992 D

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

For the exothermic reaction represented above, carried out at 298K, the rate law is as follows.

$$\text{Rate} = k[H_2][I_2]$$

Predict the effect of each of the following changes on the initial rate of the reaction and explain your prediction.

(a) Addition of hydrogen gas at constant temperature and volume

(b) Increase in volume of the reaction vessel at constant temperature

(c) Addition of catalyst. In your explanation, include a diagram of potential energy versus reaction coordinate.

(d) Increase in temperature. In your explanation, include a diagram showing the number of molecules as a function of energy.

1994 B

$$2\ NO(g) + 2\ H_2(g) \rightarrow N_2(g) + 2\ H_2O(g)$$

Experiments were conducted to study the rate of the reaction represented by the equation above. Initial concentrations and rates of reaction are given in the table below.

Experiment	Initial Concentration (mol/L) [NO]	Initial Concentration (mol/L) $[H_2]$	Initial Rate of Formation of N_2 $(mol/L\cdot min)$
1	0.0060	0.0010	1.8×10^{-4}
2	0.0060	0.0020	3.6×10^{-4}
3	0.0010	0.0060	0.30×10^{-4}
4	0.0020	0.0060	1.2×10^{-4}

(a) (i) Determine the order for each of the reactants, NO and H_2, from the data given and show your reasoning.

(ii) Write the overall rate law for the reaction.

(b) Calculate the value of the rate constant, k, for the reaction. Include units.

(c) For experiment 2, calculate the concentration of NO remaining when exactly one-half of the original amount of H_2 had been consumed.

(d) The following sequence of elementary steps is a proposed mechanism for the reaction.

I. $NO + NO \leftrightarrow N_2O_2$

II. $N_2O_2 + H_2 \rightarrow H_2O + N_2O$

III. $N_2O + H_2 \rightarrow N_2 + H_2O$

Based on the data presented, which of the above is the rate-determining step? Show that the mechanism is consistent with

(i) the observed rate law for the reaction, and

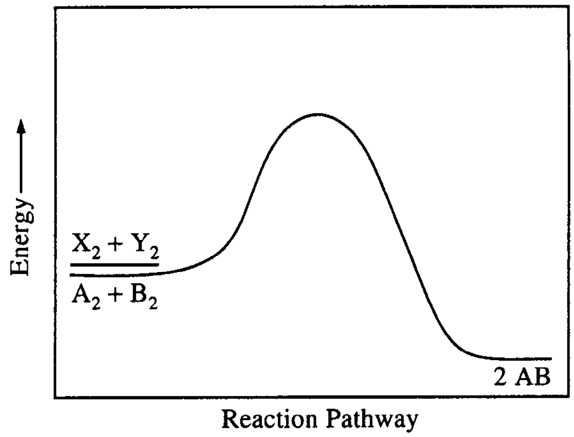
(ii) the overall stoichiometry of the reaction

1995 D

(I) $A_2 + B_2 \rightarrow 2\ AB$

(II) $X_2 + Y_2 \rightarrow 2\ XY$

Two reactions are represented above. The potential-energy diagram for reaction I is shown below. The potential energy of the reactants in reaction II is also indicated on the diagram. Reaction II is endothermic, and the activation energy of reaction I is greater than that of reaction II.



(a) Complete the potential-energy diagram for reaction II on the graph above..

(b) For reaction I, predict how each of the following is affected as the temperature is increased by 20°C. Explain the basis for each prediction.

(i) Rate of reaction

(ii) Heat of reaction

(c) For reaction II, the form of the rate law is *rate* = $k[X_2]^m[Y_2]^n$. Briefly describe an experiment that can be conducted in order to determine the values of *m* and *n* in the rate law for the reaction.

(d) From the information given, determine which reaction initially proceeds at the faster rate under the same conditions of concentration and temperature. Justify your answer.

1996 D

The reaction between NO and H_2 is believed to occur in the following three-step process.

$NO + NO \rightarrow N_2O_2$ (fast)

$N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (slow)

$N_2O + H_2 \rightarrow N_2 + H_2O$ (fast)

(a) Write a balanced equation for the overall reaction.

(b) Identify the intermediates in the reaction. Explain your reasoning.

(c) From the mechanism represented above, a student correctly deduces that the rate law for the reaction is rate = $k[NO]^2[H_2]$. The student then concludes that (1) the reaction is third-order and (2) the mechanism involves the simultaneous collision of two NO molecules and an H_2 molecule. Are conclusions (1) and (2) correct? Explain.

(d) Explain why an increase in temperature increases the rate constant, *k*, given the rate law in (c).

1997 B

$$2\ A + B \rightarrow C + D$$

The following results were obtained when the reaction represented above was studied at 25°C.

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	0.75	1.3×10^{-3}
3	1.50	1.50	5.3×10^{-3}
4	1.75	?	8.0×10^{-3}

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

(b) Write the rate law for the reaction. Calculate the value of the rate constant, specifying units.

(c) Determine the initial rate of change of [A] in Experiment 3.

(d) Determine the initial value of [B] in Experiment 4.

(e) Identify which of the reaction mechanisms represented below is consistent with the rate law developed in part (b). Justify your choice.

1. $A + B \rightarrow C + M$ *Fast*
   $M + A \rightarrow D$ *Slow*

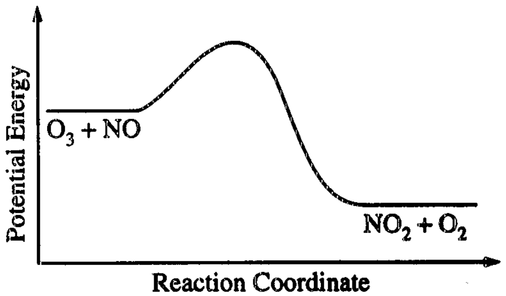
2. $B \leftrightarrow M$ *Fast equilibrium*
   $M + A \rightarrow C + X$ *Slow*
   $A + X \rightarrow D$ *Fast*

3. $A + B\ \Delta\ M$ *Fast equilibrium*
   $M + A \rightarrow C + X$ *Slow*
   $X \rightarrow D$ *Fast*

1998 D

Answer the following questions regarding the kinetics of chemical reactions.

(a) The diagram below at right shows the energy pathway for the reaction $O_3 + NO \rightarrow NO_2 + O_2$. Clearly label the following directly on the diagram.

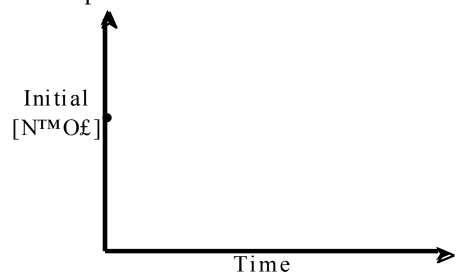


(i) The activation energy *(E_a)* for the forward reaction

(ii) The enthalpy change (ΔH) for the reaction

(b) The reaction $2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$ is first order with respect to N_2O_5.

(i) Using the axes at right, complete the graph that represents the change in $[N_2O_5]$ over time as the reaction proceeds.

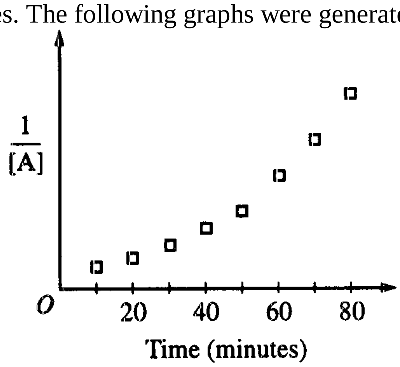


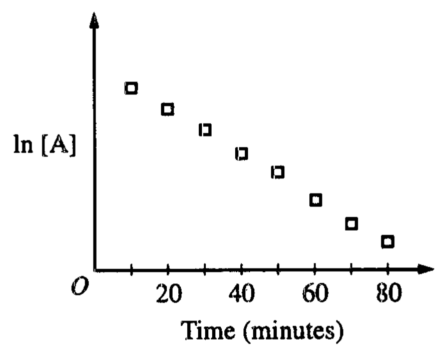
(ii) Describe how the graph in (i) could be used to find the reaction rate at a given time, *t*.

(iii) Considering the rate law and the graph in (i), describe how the value of the rate constant, *k*, could be determined.

(iv) If more N_2O_5 were added to the reaction mixture at constant temperature, what would be the effect on the rate constant, *k* ? Explain.

(c) Data for the chemical reaction $2A \rightarrow B + C$ were collected by measuring the concentration of A at 10-minute intervals for 80 minutes. The following graphs were generated from analysis of the data.





Use the information in the graphs above to answer the following.

(i) Write the rate-law expression for the reaction. Justify your answer.

(ii) Describe how to determine the value of the rate constant for the reaction.

2000 D

$O_3(g) + NO(g) \rightarrow O_2(g) + NO_2(g)$

Consider the reaction represented above.

(a) Referring to the data in the table below, calculate the standard enthalpy change, for the reaction at 25°C. Be sure to show your work.

	$O_3(g)$	$NO(g)$	$NO_2(g)$
Standard enthalpy of formation, ΔH_f° at 25°C ($kJ\ mol^{-1}$)	143	90.	33

(b) Make a qualitative prediction about the magnitude of the standard entropy change, $\Delta S°$, for the reaction at 25°C. Justify your answer.

(c) On the basis of your answers to parts (a) and (b), predict the sign of the standard free-energy change, for the reaction at 25°C. Explain your reasoning.

(d) Use the information in the table below to write the rate-law expression for the reaction, and explain how you obtained your answer.

Experiment Number	Initial $[O_3]$ ($mol\ L^{-1}$)	Initial [NO] ($mol\ L^{-1}$)	Initial Rate of Formation of $[NO_2]$ ($mol\ L^{-1}\ s^{-1}$)
1	0.0010	0.0010	x
2	0.0010	0.0020	2x
3	0.0020	0.0010	2x
4	0.0020	0.0020	4x

(e) The following three-step mechanism is proposed for the reaction. Identify the step that must be the slowest in order for this mechanism to be consistent with the rate-law expression derived in part (d). Explain.

Step I: $O_3 + NO \rightarrow O + NO_3$

Step II: $O + O_3 \rightarrow 2\ O_2$

Step III: $NO_3 + NO \rightarrow 2\ NO_2$

2002 D

An environmental concern is the depletion of O_3 in Earth's upper atmosphere, where O_3 is normally in equilibrium with O_2 and O. A proposed mechanism for the depletion of O_3 in the upper atmosphere is shown below.

Step I $O_3 + Cl \rightarrow O_2 + ClO$

Step II $ClO + O \rightarrow Cl + O_2$

(a) Write a balanced equation for the overall reaction represented by Step I and Step II above.

(b) Clearly identify the catalyst in the mechanism above. Justify your answer.

(c) Clearly identify the intermediate in the mechanism above. Justify your answer.

(d) If the rate law for the overall reaction is found to be rate = $k[O_3]$ [Cl], determine the following.

(i) The overall order of the reaction

(ii) Appropriate units for the rate constant, k

(iii) The rate-determining step of the reaction, along with justification for your answer