



NATIONAL MATH + SCIENCE INITIATIVE

AP CHEMISTRY

Kinetics—Rates and Mechanisms

2016 EDITION

Click on the following link or scan the QR code
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https://www.surveymonkey.com/r/S_SSS



Periodic Table of the Elements

1 H 1.0079																	2 He 4.0026						
3 Li 6.941	4 Be 9.012															9 F 19.00	10 Ne 20.179						
11 Na 22.99	12 Mg 24.30	13 Al 26.98	14 Si 28.09	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948																
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.938	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80						
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 93.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.91	54 Xe 131.29						
55 Cs 132.91	56 Ba 137.33	57 *La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.2	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)						
87 Fr (223)	88 Ra 226.02	89 †Ac 227.03	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 S (269)	111 S (272)	112 S (277)	§Not yet named											

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.4	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

*Lanthanide Series:

†Actinide Series:

AP Chemistry Equations & Constants

Throughout the test the following symbols have the definitions specified unless otherwise noted.

L, mL = liter(s), milliliter(s)

g = gram(s)

nm = nanometer(s)

atm = atmosphere(s)

mm Hg = millimeters of mercury

J, kJ = joule(s), kilojoule(s)

V = volt(s)

mol = mole(s)

ATOMIC STRUCTURE

$$E = h\nu$$

$$c = \lambda\nu$$

E = energy

ν = frequency

λ = wavelength

Planck's constant, $h = 6.626 \times 10^{-34}$ J s

Speed of light, $c = 2.998 \times 10^8$ m s⁻¹

Avogadro's number = 6.022×10^{23} mol⁻¹

Electron charge, $e = -1.602 \times 10^{-19}$ coulomb

EQUILIBRIUM

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}, \text{ where } a A + b B \rightleftharpoons c C + d D$$

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

$$= K_a \times K_b$$

$$\text{pH} = -\log [H^+], \text{ pOH} = -\log [OH^-]$$

$$14 = \text{pH} + \text{pOH}$$

$$\text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]}$$

$$\text{p}K_a = -\log K_a, \text{ p}K_b = -\log K_b$$

Equilibrium Constants

K_c (molar concentrations)

K_p (gas pressures)

K_a (weak acid)

K_b (weak base)

K_w (water)

KINETICS

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$t_{1/2} = \frac{0.693}{k}$$

k = rate constant

t = time

$t_{1/2}$ = half-life

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$P_A = P_{\text{total}} \times X_A, \text{ where } X_A = \frac{\text{moles A}}{\text{total moles}}$$

$$P_{\text{total}} = P_A + P_B + P_C + \dots$$

$$n = \frac{m}{M}$$

$$K = ^\circ\text{C} + 273$$

$$D = \frac{m}{V}$$

$$KE \text{ per molecule} = \frac{1}{2}mv^2$$

Molarity, M = moles of solute per liter of solution

$$A = abc$$

P = pressure

V = volume

T = temperature

n = number of moles

m = mass

M = molar mass

D = density

KE = kinetic energy

v = velocity

A = absorbance

a = molar absorptivity

b = path length

c = concentration

Gas constant, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$$= 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$= 62.36 \text{ L torr mol}^{-1} \text{ K}^{-1}$$

1 atm = 760 mm Hg

$$= 760 \text{ torr}$$

STP = 0.00°C and 1.000 atm

THERMOCHEMISTRY/ ELECTROCHEMISTRY

$$q = mc\Delta T$$

$$\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -RT \ln K$$

$$= -nFE^\circ$$

$$I = \frac{q}{t}$$

q = heat

m = mass

c = specific heat capacity

T = temperature

S° = standard entropy

H° = standard enthalpy

G° = standard free energy

n = number of moles

E° = standard reduction potential

I = current (amperes)

q = charge (coulombs)

t = time (seconds)

Faraday's constant, $F = 96,485$ coulombs per mole of electrons

$$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$$



What I Absolutely Have to Know to Survive the AP Exam

The following might indicate the question deals with kinetics: rate; reactant concentration; order; rate constant; mechanisms; rate determining step; intermediate; catalyst; half-life; instantaneous rate; relative rate; activation energy; integrated rate law; rate expression; rate law

FACTORS THAT AFFECT REACTION RATE

Temperature	Reaction rate increases with increasing temperature – “heat `em up, speed `em up” The higher the temp the more likely there are more collisions that are able to overcome the activation energy and form products
Nature of the Reactants	Phases of matter play a role, chemical identity (ions of opposite charge typically react faster; molecules with more bonds to break and form and substances with stronger bonds react more slowly)
Concentration of the Reactants	Reaction rate typically increases with increasing concentration of reactants (pressure changes have the same effect on gaseous reactions) – more reactants the more effective collisions, the faster the reactions proceeds
Catalyst	Reaction rate increases with the addition of a catalyst; not a part of the reaction and is not used up but typically participates in the rate determining step of the reaction (slowest step) – it LOWERS the activation energy!
Surface Area	Reaction rate increases with increased surface area of the reactant; reactions occur at the exposed surface of the two substances (except in <i>g</i> or <i>aq</i>) thus the greater the surface area the more exposure the greater chance of effective collisions, the greater the rate. Aqueous solutions offer the ultimate exposure.
Inert Gas	DON'T FALL FOR THIS – adding an inert gas will NOT effect the reaction rate; it is not part of the reaction mechanism thus is has NO EFFECT

Collision Theory of Reactions

For a reaction to happen two things must occur:

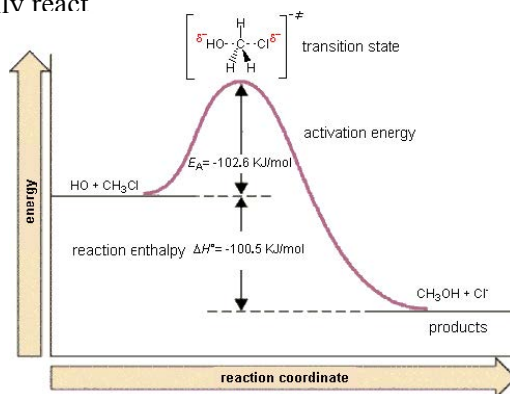
1. The molecules must collide with the appropriate orientation for a reaction to occur
2. Molecules must collide with enough kinetic energy to react – i.e. they must meet or exceed the energy of activation, E_a

In other words the collisions **MUST BE EFFECTIVE**.

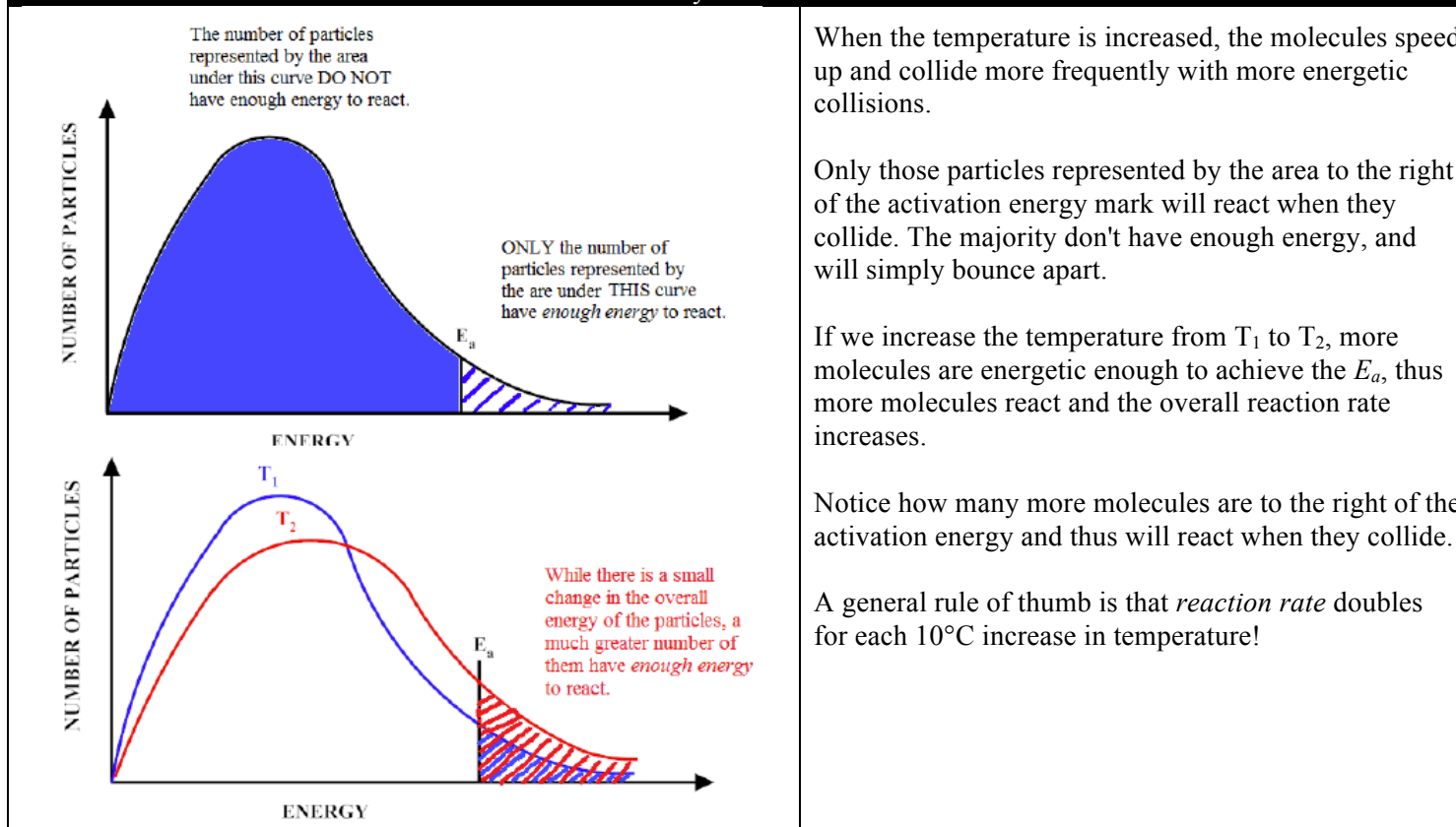
If this happens the product of an effective collision is at the peak of the energy hump (activated complex or the transition state. This complex can either fall back to reactants or produce products

E_a – the activation energy...

- Is a measure of the energy barrier colliding molecules must overcome if they are to react rather than recoil from one another.
- It is assumed that reacting species with energy less than E_a will not react and those with energy greater than E_a and the proper orientation will typically react



Collision Theory of Reactions Con't...

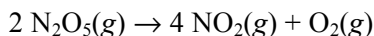


EXPRESSING REACTION RATE

Reaction rate is expressed in terms of how fast the concentration of a substance changes. It does not matter whether you measure the rate the products are formed or the rate at which the reactants are consumed – they are stoichiometrically linked – just focus on *either* the disappearance of the reactants (–) or the appearance of the (+).

$$\text{Rate of reaction} = \frac{\Delta[\text{product}]}{\text{time}} \text{ or Rate of reaction} = - \frac{\Delta[\text{reactant}]}{\text{time}}$$

For example:



The relative rate can be expressed as:

$$\text{rate} = -\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

Translated...

- The rate of consumption (disappearance) of N_2O_5 is equal to half the rate of the production (appearance) of NO_2 and equal to twice the production (appearance) of O_2

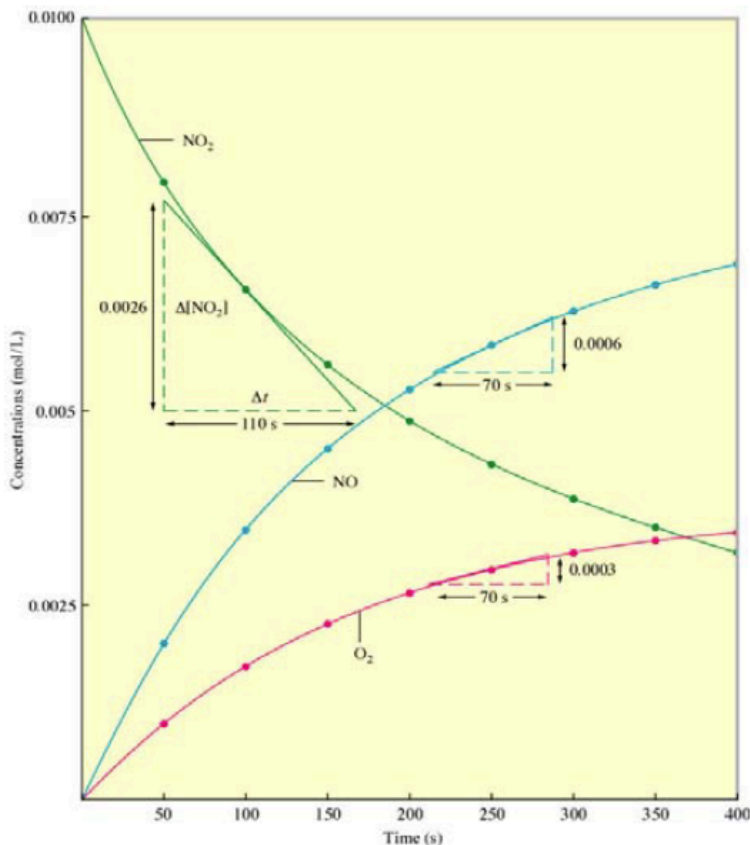
Or better yet...

- NO_2 is produced at twice the rate at which N_2O_5 is consumed
- O_2 is produced at half the rate at which N_2O_5 is consumed



Instantaneous Rate

Instantaneous rate is the rate at any one point in time during the experiment. To find instantaneous reaction rate you find the slope of the curve at the time in question (for those of you in calculus aka...derivative) i.e. the slope of the tangent line to that point in time.

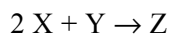


Differential Rate Laws – Concentration and Rate

The rate law is a mathematical equation relating the instantaneous **rate** at a particular point in the progress of a chemical reaction to the **concentration** of the reacting species.

- Rate generally refers to the **initial** rate.
- The initial rate is the fastest rate of the reaction and occurs at the very beginning of the reaction.
- At this point there are few competing reactions, little chance for the reverse reaction (think equilibrium) to get involved, etc.
- It should be noted when using the initial rate the concentration of the reactants are initial concentrations.

For the following reaction...



the general form of the rate law is...

$$\text{rate} = k[X]^m [Y]^n$$

Where...

- k is the rate constant
- The exponent m represents the order of the reaction with respect to reactant X
- The exponent n represents the order of the reaction with respect to reactant Y
- The sum of $m + n$ represents the overall order of the reaction.

Reactant orders must be determined experimentally; they cannot be written from the overall balanced equation



Differential Rate Laws – Concentration and Rate Con't...

Using the experimental data shown below you can determine the order of each reactant, the overall reaction order, and calculate the rate constant, k .

Experiment Number	Initial Rate mol/(L•hr)	Initial concentration [A] ₀	Initial concentration [B] ₀
1	0.50×10^{-2}	0.50	0.20
2	0.50×10^{-2}	0.75	0.20
3	0.50×10^{-2}	1.00	0.20
4	1.00×10^{-2}	0.50	0.40
5	1.50×10^{-2}	0.50	0.60

Examine the data with an analytical eye. Look for two trials where the concentration of ONE reactant was held constant. Then compare how the other reactant changed and its effect on the initial rate.

- Look at Experiments 1 & 4
[A] was held constant and [B] doubled – the initial rate of the reaction doubled, therefore the reaction is *FIRST ORDER* with respect to reactant B.
- Look at Experiments 1 & 3
[B] was held constant and [A] doubled – the initial rate of the reaction was unchanged, therefore the reaction is *ZERO ORDER* with respect to reactant A.
- Use experiment 5 (can use any of them) to solve for the rate constant, k .

$$\text{rate} = k[A]^0[B]^1$$

or

$$\text{rate} = k[B]$$

$$\text{rate} = k[B]$$

$$\frac{\text{rate}}{[B]} = k = \frac{1.50 \times 10^{-2}}{0.60} = 0.025 \text{ hr}^{-1}$$

Reaction Mechanisms

Reaction mechanisms attempt to describe the stepwise sequence of elementary reactions that take reactants to products. The mechanism describes in detail the bonds that are broken and formed as the reaction proceeds.

Each elementary step of a mechanism typically involves one or two reactants forming products.

Every mechanism consists of a series of stepwise reactions. Each reaction in the mechanism has a rate associated with it.

The overall speed of the reaction depends upon the slowest step of the mechanism. The rate law of this step is identical or equivalent to the experimental rate law. The slow step of the mechanism is also called the rate-determining step of the mechanism. The sum of all the steps of the mechanism must equal the overall balanced chemical equation.

The coefficients of the reactants in the rate-determining step of the mechanism must correspond to the exponents or order of the reactants in the experimental rate law.

Catalysts and Intermediates...

- A catalyst is used up early in a reaction (reactant) and is regenerated (product) in a subsequent step.
- A catalyst is a substance that acts to increase the rate of a chemical reaction by providing an alternate path for the reaction to occur. This means that there will be a change in the magnitude of the rate constant and possibly a change in the order of the reaction.
- An intermediate is produced early in the reaction (product) and used up (reactant) in a subsequent step.

Kinetics Cheat Sheet

RelationshipsDifferential Rate Law (concentration vs. rate data): $\text{Rate} = k [A]^x[B]^y$

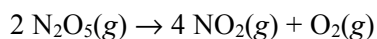
Be able to explain with algebraic equations or words how an order is determined. It is important to state which concentration(s) is/are held constant and which concentration is varied as well the effect that has on the rate of the reaction if you choose not to justify with algebraic equations.

Mechanisms – must agree with the stoichiometry of the reaction and the “summary rate law” must agree with the slow step; identify intermediates and catalysts and clearly state that the correct mechanism “agrees with the experimentally determined rate law”.

Discuss number of *effective collisions* in relation to increasing or decreasing rates

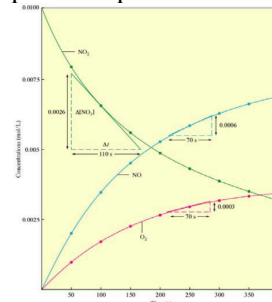
E_a predicts speed but the relationship is an inverse one; high = slow rate; low = fast rate

“rate in terms of” is code for “relative rates” – use stoichiometry ratios on rate value



$$\text{rate} = -\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

Instantaneous rate = slope of the line tangent to the time point in question



Catalyst – lowers Activation Energy and provides an alternate pathway/mechanism

Distinguish between catalyst and intermediate – especially in the steps of a mechanism!

Temperature increases of approx.. 10°C

Connections

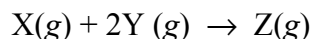
Stoichiometry – “using up” one component of the system might indicate a limiting reactant in effect

Electrochemistry – if reaction is redox in nature, rate problems could come into play

Thermochemistry – E_a and $\Delta H^\circ_{\text{rxn}}$ and reaction diagrams

Potential Pitfalls

Units on k ! Make sure you can solve for units for k

NMSI SUPER PROBLEM

The reaction represented above was studied at 25°C. The data collected are shown in the table below.

Experiment	[X]	[Y]	Initial rate of formation of Z (mol L ⁻¹ sec ⁻¹)
1	0.200	0.200	1.20×10^{-5}
2	0.200	0.400	2.40×10^{-5}
3	0.100	0.200	6.00×10^{-6}

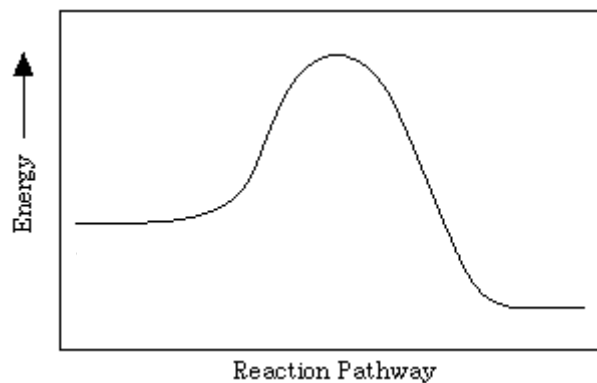
- (a) Calculate the initial rate of disappearance of substance Y in Experiment 1.
- (b) Determine the order of the reaction with respect to each reactant. Show your work.
- X
 - Y
- (c) Write the rate law for the reaction consistent with part B.
- (d) Calculate the value of the rate constant, k . Be sure to include proper units.
- (e) In a closed 2.50 L reaction vessel at 22°C, 0.0254 mole of substance X was reacted with 0.0495 mol Y
- Determine the limiting reactant. Justify your answer mathematically.
 - Calculate the number of moles of Z formed.
 - Calculate the total pressure in the flask at the completion of the reaction.
- (f) Three possible mechanisms for this reaction are shown below.

Mechanism 1	Mechanism 2	Mechanism 3
Y + Y \rightleftharpoons D (fast)	X \rightarrow D (slow)	X + Y \rightarrow D (slow)
X + D \rightarrow Z (slow)	D + Y \rightarrow G (fast)	Y + D \rightarrow Z (fast)
	G + Y \rightarrow Z (fast)	

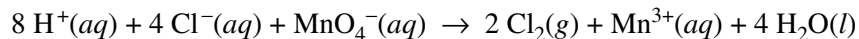
- Select the one most consistent with the experimental data. Justify your choice by writing a rate law for each of the three mechanisms.
- Identify substance D in the mechanisms shown above as an intermediate or a catalyst. Justify your answer.



- (g) The following diagram shows the energy of the reaction as the reaction progresses.
- Clearly label the activation energy for the forward reaction.
 - Clearly label the enthalpy change for the reaction.
 - On the diagram draw a second energy curve showing the effect of a catalyst on the reaction.



- (h) The collision between X and Y occur with enough energy to overcome the activation energy barrier, E_a , however no products are formed. Identify and explain one other factor that affects whether the collision will result in a reaction.

2010 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS

3. $\text{Cl}_2(g)$ can be generated in the laboratory by reacting potassium permanganate with an acidified solution of sodium chloride. The net-ionic equation for the reaction is given above.
- (a) A 25.00 mL sample of 0.250 M NaCl reacts completely with excess $\text{KMnO}_4(aq)$. The $\text{Cl}_2(g)$ produced is dried and stored in a sealed container. At 22°C the pressure of the $\text{Cl}_2(g)$ in the container is 0.950 atm.
- (i) Calculate the number of moles of $\text{Cl}^-(aq)$ present before any reaction occurs.
- (ii) Calculate the volume, in L, of the $\text{Cl}_2(g)$ in the sealed container.

An initial-rate study was performed on the reaction system. Data for the experiment are given in the table below.

Trial	$[\text{Cl}^-]$	$[\text{MnO}_4^-]$	$[\text{H}^+]$	Rate of Disappearance of MnO_4^- in $M \text{ s}^{-1}$
1	0.0104	0.00400	3.00	2.25×10^{-8}
2	0.0312	0.00400	3.00	2.03×10^{-7}
3	0.0312	0.00200	3.00	1.02×10^{-7}

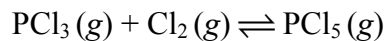
- (b) Using the information in the table, determine the order of the reaction with respect to each of the following. Justify your answers.
- (i) Cl^-
- (ii) MnO_4^-
- (c) The reaction is known to be third order with respect to H^+ . Using this information and your answers to part (b) above, complete both of the following:
- (i) Write the rate law for the reaction.
- (ii) Calculate the value of the rate constant, k , for the reaction, including appropriate units.
- (d) Is it likely that the reaction occurs in a single elementary step? Justify your answer.

S T O P

**If you finish before time is called, you may check your work on this part only.
Do not turn to the other part of the test until you are told to do so.**

1985 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS*ADAPTED for a Short Free Response*

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



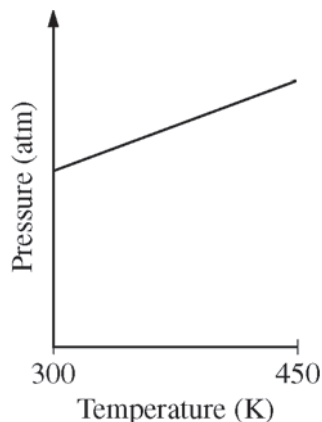
- (a) Suppose that 2 moles of PCl_3 and 1 mole of Cl_2 are mixed in a closed container at constant temperature. Draw a graph that shows how the concentrations of PCl_3 , Cl_2 , and PCl_5 change with time until after equilibrium has been firmly established.
- (b) Provide a molecular explanation for the dependence of the rate of the forward reaction on
- the concentrations of the reactants
 - temperature

2013 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS

Answer Question 5 and Question 6. The Section II score weighting for these questions is 15 percent each.

Your responses to these questions will be scored on the basis of the accuracy and relevance of the information cited. Explanations should be clear and well organized. Examples and equations may be included in your responses where appropriate. Specific answers are preferable to broad, diffuse responses.

5. A sample of $C_2H_4(g)$ is placed in a previously evacuated, rigid 2.0 L container and heated from 300 K to 450 K. The pressure of the sample is measured and plotted in the graph below.



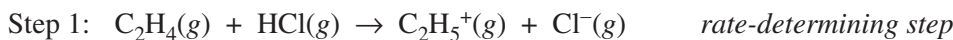
- (a) Describe TWO reasons why the pressure changes as the temperature of the $C_2H_4(g)$ increases. Your descriptions must be in terms of what occurs at the molecular level.

$C_2H_4(g)$ reacts readily with $HCl(g)$ to produce $C_2H_5Cl(g)$, as represented by the following equation.



- (b) When $HCl(g)$ is injected into the container of $C_2H_4(g)$ at 450 K, the total pressure increases. Then, as the reaction proceeds at 450 K, the total pressure decreases. Explain this decrease in total pressure in terms of what occurs at the molecular level.

It is proposed that the formation of $C_2H_5Cl(g)$ proceeds via the following two-step reaction mechanism.



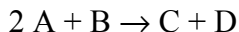
- (c) Write the rate law for the reaction that is consistent with the reaction mechanism above.
- (d) Identify an intermediate in the reaction mechanism above.

2013 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS

- (e) Using the axes provided below, draw a curve that shows the energy changes that occur during the progress of the reaction. The curve should illustrate both the proposed two-step mechanism and the enthalpy change of the reaction.



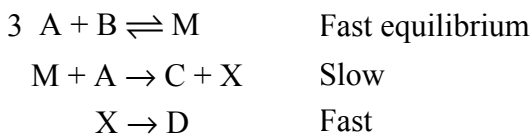
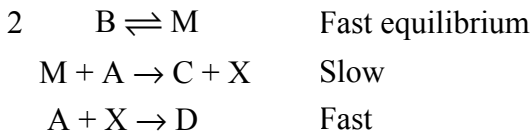
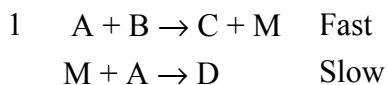
- (f) On the diagram above, clearly indicate the activation energy, E_a , for the rate-determining step in the reaction.

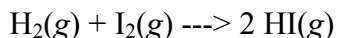
1997 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS

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 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.



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

$$\text{Rate} = k [\text{H}_2] [\text{I}_2]$$

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 a 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.