AP® Chemistry
2014 Free-Response Questions

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PERIODIC TABLE OF THE ELEMENTS

1 **H** 1.008																	2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.30											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.95
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** 54.94	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** 95.94	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** (266)	107 **Bh** (264)	108 **Hs** (277)	109 **Mt** (268)	110 **Ds** (271)	111 **Rg** (272)							

*Lanthanide Series	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
†Actinide Series	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** (237)	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** (262)

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AP® CHEMISTRY EQUATIONS AND CONSTANTS

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

L, mL	=	liter(s), milliliter(s)	mm Hg	=	millimeters of mercury
g	=	gram(s)	J, kJ	=	joule(s), kilojoule(s)
nm	=	nanometer(s)	V	=	volt(s)
atm	=	atmosphere(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

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

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

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

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

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

$= K_a \times K_b$

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

$14 = pH + pOH$

$pH = pK_a + \log\dfrac{[A^-]}{[HA]}$

$pK_a = -\log K_a$, $pK_b = -\log K_b$

Equilibrium Constants

K_c (molar concentrations)
K_p (gas pressures)
K_a (weak acid)
K_b (weak base)
K_w (water)

KINETICS

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

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

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

k = rate constant
t = time
$t_{1/2}$ = half-life

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GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

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

$$P_{total} = P_A + P_B + P_C + \ldots$$

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

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

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

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

Molarity, M = moles of solute per liter of solution

$$A = abc$$

P = pressure
V = volume
T = temperature
n = number of moles
m = mass
$\boldsymbol{M}$ = 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 torr

STP = 273.15 K and 1.0 atm

THERMODYNAMICS / 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 Gibbs 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

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

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CHEMISTRY
Section II
7 Questions
Time—90 minutes

YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.

Directions: Questions 1–3 are long free-response questions that require about 20 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 7 minutes each to answer and are worth 4 points each.

Write your response in the space provided following each question. Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved in arriving at your answers. You must show your work to receive credit for your answer. Pay attention to significant figures.

Mass of KI tablet	0.425 g
Mass of thoroughly dried filter paper	1.462 g
Mass of filter paper + precipitate after first drying	1.775 g
Mass of filter paper + precipitate after second drying	1.699 g
Mass of filter paper + precipitate after third drying	1.698 g

1. A student is given the task of determining the I^- content of tablets that contain KI and an inert, water-soluble sugar as a filler. A tablet is dissolved in 50.0 mL of distilled water, and an excess of 0.20 *M* $Pb(NO_3)_2(aq)$ is added to the solution. A yellow precipitate forms, which is then filtered, washed, and dried. The data from the experiment are shown in the table above.

   (a) For the chemical reaction that occurs when the precipitate forms,

   (i) write a balanced, net-ionic equation for the reaction, and

   (ii) explain why the reaction is best represented by a net-ionic equation.

   (b) Explain the purpose of drying and weighing the filter paper with the precipitate three times.

   (c) In the filtrate solution, is $[K^+]$ greater than, less than, or equal to $[NO_3^-]$? Justify your answer.

   (d) Calculate the number of moles of precipitate that is produced in the experiment.

   (e) Calculate the mass percent of I^- in the tablet.

   (f) In another trial, the student dissolves a tablet in 55.0 mL of water instead of 50.0 mL of water. Predict whether the experimentally determined mass percent of I^- will be greater than, less than, or equal to the amount calculated in part (e). Justify your answer.

(g) A student in another lab also wants to determine the I^- content of a KI tablet but does not have access to $Pb(NO_3)_2$. However, the student does have access to 0.20 *M* $AgNO_3$, which reacts with $I^-(aq)$ to produce $AgI(s)$. The value of K_{sp} for AgI is 8.5×10^{-17}.

(i) Will the substitution of $AgNO_3$ for $Pb(NO_3)_2$ result in the precipitation of the I^- ion from solution? Justify your answer.

(ii) The student only has access to one KI tablet and a balance that can measure to the nearest 0.01 g. Will the student be able to determine the mass of AgI produced to three significant figures? Justify your answer.

$$CH_3CH_2COOH(aq) + H_2O(l) \rightleftarrows CH_3CH_2COO^-(aq) + H_3O^+(aq)$$

2. Propanoic acid, CH_3CH_2COOH, is a carboxylic acid that reacts with water according to the equation above. At 25°C the pH of a 50.0 mL sample of 0.20 *M* CH_3CH_2COOH is 2.79.

   (a) Identify a Brønsted-Lowry conjugate acid-base pair in the reaction. Clearly label which is the acid and which is the base.

   (b) Determine the value of K_a for propanoic acid at 25°C.

   (c) For each of the following statements, determine whether the statement is true or false. In each case, explain the reasoning that supports your answer.

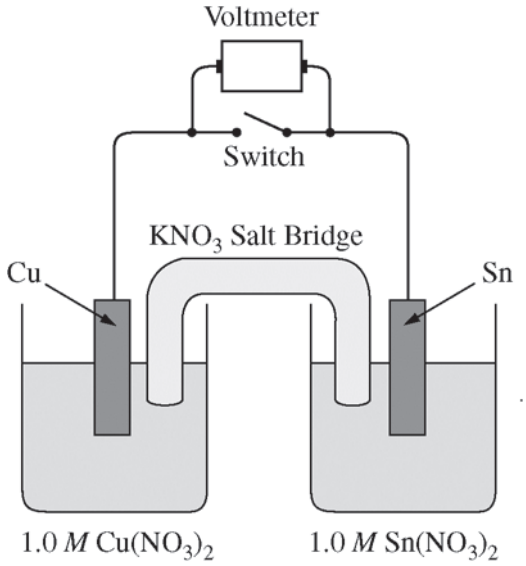
      (i) The pH of a solution prepared by mixing the 50.0 mL sample of 0.20 *M* CH_3CH_2COOH with a 50.0 mL sample of 0.20 *M* NaOH is 7.00.

      (ii) If the pH of a hydrochloric acid solution is the same as the pH of a propanoic acid solution, then the molar concentration of the hydrochloric acid solution must be less than the molar concentration of the propanoic acid solution.

   A student is given the task of determining the concentration of a propanoic acid solution of unknown concentration. A 0.173 *M* NaOH solution is available to use as the titrant. The student uses a 25.00 mL volumetric pipet to deliver the propanoic acid solution to a clean, dry flask. After adding an appropriate indicator to the flask, the student titrates the solution with the 0.173 *M* NaOH, reaching the end point after 20.52 mL of the base solution has been added.

   (d) Calculate the molarity of the propanoic acid solution.

   (e) The student is asked to redesign the experiment to determine the concentration of a butanoic acid solution instead of a propanoic acid solution. For butanoic acid the value of pK_a is 4.83. The student claims that a different indicator will be required to determine the equivalence point of the titration accurately. Based on your response to part (b), do you agree with the student's claim? Justify your answer.

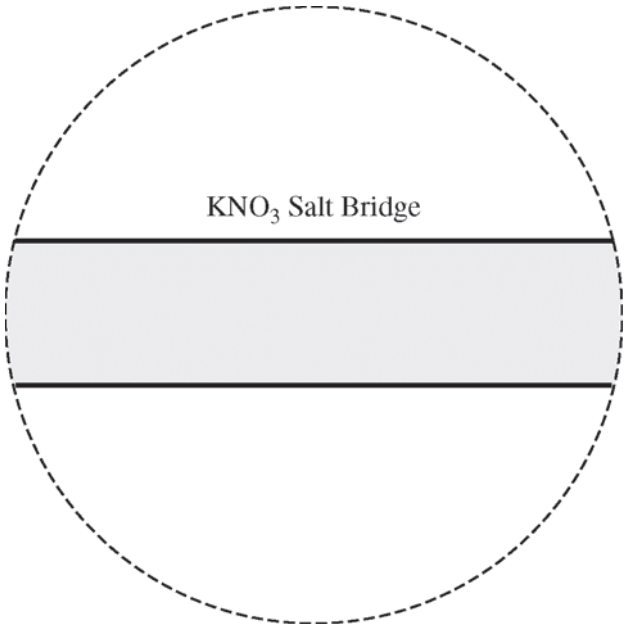


3. A student is given a standard galvanic cell, represented above, that has a Cu electrode and a Sn electrode. As current flows through the cell, the student determines that the Cu electrode increases in mass and the Sn electrode decreases in mass.

   (a) Identify the electrode at which oxidation is occurring. Explain your reasoning based on the student's observations.

   (b) As the mass of the Sn electrode decreases, where does the mass go?

   (c) In the expanded view of the center portion of the salt bridge shown in the diagram below, draw and label a particle view of what occurs in the salt bridge as the cell begins to operate. Omit solvent molecules and use arrows to show the movement of particles.



(d) A nonstandard cell is made by replacing the 1.0 *M* solutions of $Cu(NO_3)_2$ and $Sn(NO_3)_2$ in the standard cell with 0.50 *M* solutions of $Cu(NO_3)_2$ and $Sn(NO_3)_2$. The volumes of solutions in the nonstandard cell are identical to those in the standard cell.

(i) Is the cell potential of the nonstandard cell greater than, less than, or equal to the cell potential of the standard cell? Justify your answer.

(ii) Both the standard and nonstandard cells can be used to power an electronic device. Would the nonstandard cell power the device for the same time, a longer time, or a shorter time as compared with the standard cell? Justify your answer.

(e) In another experiment, the student places a new Sn electrode into a fresh solution of 1.0 *M* $Cu(NO_3)_2$.

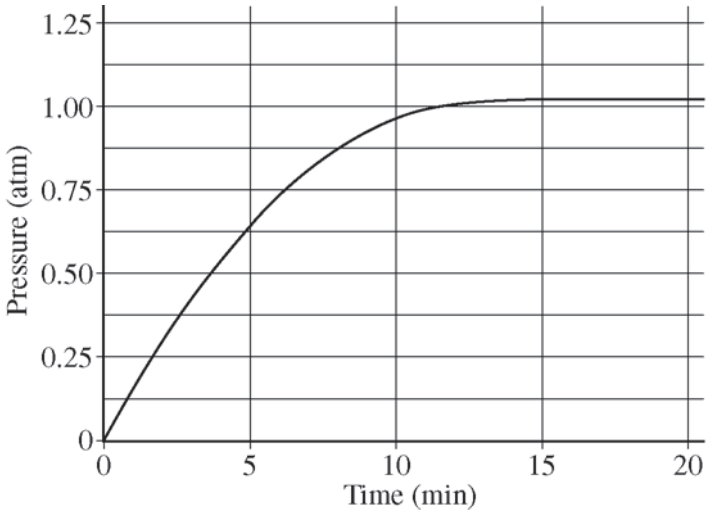
Half-Reaction	$E°$ (V)
$Cu^+ + e^- \rightarrow Cu(s)$	0.52
$Cu^{2+} + 2\,e^- \rightarrow Cu(s)$	0.34
$Sn^{4+} + 2\,e^- \rightarrow Sn^{2+}$	0.15
$Sn^{2+} + 2\,e^- \rightarrow Sn(s)$	–0.14

(i) Using information from the table above, write a net-ionic equation for the reaction between the Sn electrode and the $Cu(NO_3)_2$ solution that would be thermodynamically favorable. Justify that the reaction is thermodynamically favorable.

(ii) Calculate the value of $\Delta G°$ for the reaction. Include units with your answer.

$$CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$$

4. When heated, calcium carbonate decomposes according to the equation above. In a study of the decomposition of calcium carbonate, a student added a 50.0 g sample of powdered $CaCO_3(s)$ to a 1.00 L rigid container. The student sealed the container, pumped out all the gases, then heated the container in an oven at 1100 K. As the container was heated, the total pressure of the $CO_2(g)$ in the container was measured over time. The data are plotted in the graph below.



The student repeated the experiment, but this time the student used a 100.0 g sample of powdered $CaCO_3(s)$. In this experiment, the final pressure in the container was 1.04 atm, which was the same final pressure as in the first experiment.

(a) Calculate the number of moles of $CO_2(g)$ present in the container after 20 minutes of heating.

(b) The student claimed that the final pressure in the container in each experiment became constant because all of the $CaCO_3(s)$ had decomposed. Based on the data in the experiments, do you agree with this claim? Explain.

(c) After 20 minutes some $CO_2(g)$ was injected into the container, initially raising the pressure to 1.5 atm. Would the final pressure inside the container be less than, greater than, or equal to 1.04 atm? Explain your reasoning.

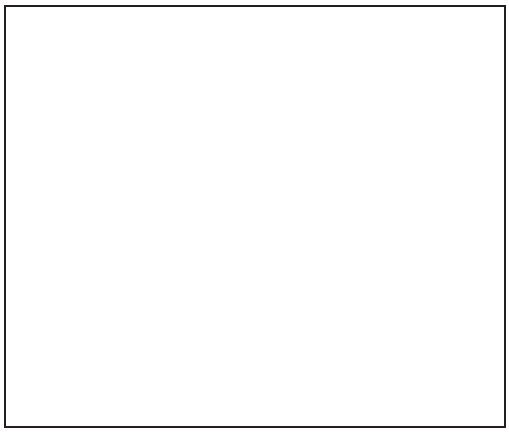
(d) Are there sufficient data obtained in the experiments to determine the value of the equilibrium constant, K_p, for the decomposition of $CaCO_3(s)$ at 1100 K? Justify your answer.

Nonmetal	C	N	O	Ne	Si	P	S	Ar
Formula of Compound	CF_4	NF_3	OF_2	No compound	SiF_4	PF_3	SF_2	No compound

5. Some binary compounds that form between fluorine and various nonmetals are listed in the table above. A student examines the data in the table and poses the following hypothesis: the number of F atoms that will bond to a nonmetal is always equal to 8 minus the number of valence electrons in the nonmetal atom.

   (a) Based on the student's hypothesis, what should be the formula of the compound that forms between chlorine and fluorine?

   (b) In an attempt to verify the hypothesis, the student researches the fluoride compounds of the other halogens and finds the formula ClF_3. In the box below, draw a complete Lewis electron-dot diagram for a molecule of ClF_3.



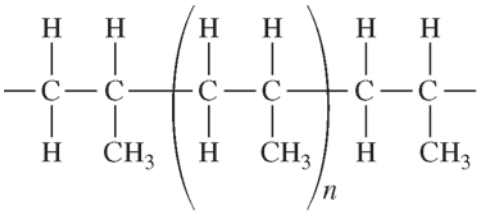
   (c) Two possible geometric shapes for the ClF_3 molecule are trigonal planar and T-shaped. The student does some research and learns that the molecule has a dipole moment. Which of the two shapes is consistent with the fact that the ClF_3 molecule has a dipole moment? Justify your answer in terms of bond polarity and molecular structure.

In an attempt to resolve the existence of the ClF_3 molecule with the hypothesis stated above, the student researches the compounds that form between halogens and fluorine, and assembles the following list.

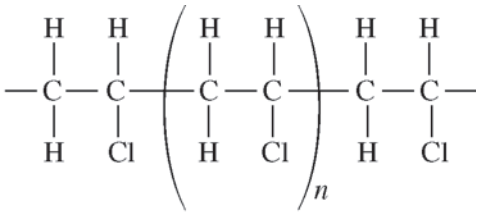
Halogen	Formula(s)
F	F_2
Cl	
Br	BrF, BrF_3, BrF_5
I	IF, IF_3, IF_5, IF_7

   (d) Based on concepts of atomic structure and periodicity, propose a modification to the student's previous hypothesis to account for the compounds that form between halogens and fluorine.

6. A student places a mixture of plastic beads consisting of polypropylene (PP) and polyvinyl chloride (PVC) in a 1.0 L beaker containing distilled water. After stirring the contents of the beaker vigorously, the student observes that the beads of one type of plastic sink to the bottom of the beaker and the beads of the other type of plastic float on the water. The chemical structures of PP and PVC are represented by the diagrams below, which show segments of each polymer.



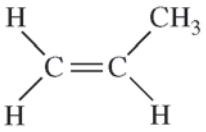
PP



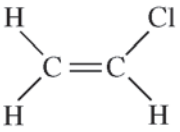
PVC

(a) Given that the spacing between polymer chains in PP and PVC is similar, the beads that sink are made of which polymer? Explain.

PP is synthesized from propene, C_3H_6, and PVC is synthesized from vinyl chloride, C_2H_3Cl. The structures of the molecules are shown below.



Propene



Vinyl Chloride (chloroethene)

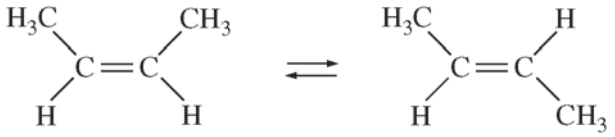
(b) The boiling point of liquid propene (226 K) is lower than the boiling point of liquid vinyl chloride (260 K). Account for this difference in terms of the types and strengths of intermolecular forces present in each liquid.

In a separate experiment, the student measures the enthalpies of combustion of propene and vinyl chloride. The student determines that the combustion of 2.00 mol of vinyl chloride releases 2300 kJ of energy, according to the equation below.

$$2\ C_2H_3Cl(g)\ +\ 5\ O_2(g)\ \rightarrow\ 4\ CO_2(g)\ +\ 2\ H_2O(g)\ +\ 2\ HCl(g) \qquad \Delta H^\circ = -2300\ \text{kJ/mol}_{rxn}$$

(c) Using the table of standard enthalpies of formation below, determine whether the combustion of 2.00 mol of propene releases more, less, or the same amount of energy that 2.00 mol of vinyl chloride releases. Justify your answer with a calculation. The balanced equation for the combustion of 2.00 mol of propene is $2\ C_3H_6(g)\ +\ 9\ O_2(g)\ \rightarrow\ 6\ CO_2(g)\ +\ 6\ H_2O(g)$.

Substance	$C_2H_3Cl(g)$	$C_3H_6(g)$	$CO_2(g)$	$H_2O(g)$	$HCl(g)$	$O_2(g)$
Standard Enthalpy of Formation (kJ/mol)	37	21	–394	–242	–92	0



cis-2-butene ⇌ *trans*-2-butene

7. The half-life ($t_{1/2}$) of the catalyzed isomerization of *cis*-2-butene gas to produce *trans*-2-butene gas, represented above, was measured under various conditions, as shown in the table below.

Trial Number	Initial $P_{cis\text{-}2\text{-butene}}$ (torr)	V (L)	T (K)	$t_{1/2}$ (s)
1	300.	2.00	350.	100.
2	600.	2.00	350.	100.
3	300.	4.00	350.	100.
4	300.	2.00	365	50.

(a) The reaction is first order. Explain how the data in the table are consistent with a first-order reaction.

(b) Calculate the rate constant, k, for the reaction at 350. K. Include appropriate units with your answer.

(c) Is the initial rate of the reaction in trial 1 greater than, less than, or equal to the initial rate in trial 2? Justify your answer.

(d) The half-life of the reaction in trial 4 is less than the half-life in trial 1. Explain why, in terms of activation energy.

STOP

END OF EXAM