2019

AP® CollegeBoard

AP® Chemistry

Free-Response Questions

This version of the 2019 Free Response Questions has been modified to reflect the layout that will be used on the 2020 AP Chemistry Exam.

Additionally, the Periodic Table and the Equations and Constants pages have been updated to match those on the 2020 AP Chemistry Exam.

DO NOT DETACH FROM BOOK.

PERIODIC TABLE OF THE ELEMENTS

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
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** 47.87	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** 65.38	31 **Ga** 69.72	32 **Ge** 72.63	33 **As** 74.92	34 **Se** 78.97	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** 95.95	43 **Tc**	44 **Ru** 101.07	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** 121.76	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	57–71 *	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.84	75 **Re** 186.21	76 **Os** 190.23	77 **Ir** 192.22	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**	85 **At**	86 **Rn**
87 **Fr**	88 **Ra**	89–103 †	104 **Rf**	105 **Db**	106 **Sg**	107 **Bh**	108 **Hs**	109 **Mt**	110 **Ds**	111 **Rg**	112 **Cn**	113 **Nh**	114 **Fl**	115 **Mc**	116 **Lv**	117 **Ts**	118 **Og**

*Lanthanoids	57 **La** 138.91	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm**	62 **Sm** 150.36	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** 173.05	71 **Lu** 174.97
†Actinoids	89 **Ac**	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np**	94 **Pu**	95 **Am**	96 **Cm**	97 **Bk**	98 **Cf**	99 **Es**	100 **Fm**	101 **Md**	102 **No**	103 **Lr**

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

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

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

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

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

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

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

$$14 = pH + pOH$$

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

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

Equilibrium Constants

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

KINETICS

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

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

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

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

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

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

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

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

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

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

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

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

Molarity, M = moles of solute per liter of solution

$$A = \varepsilon bc$$

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
ε = molar absorptivity
b = path length
c = concentration

Gas constant, R = 8.314 J $\text{mol}^{-1}\,\text{K}^{-1}$
= 0.08206 L atm $\text{mol}^{-1}\,\text{K}^{-1}$
= 62.36 L torr $\text{mol}^{-1}\,\text{K}^{-1}$

1 atm = 760 mm Hg = 760 torr

STP = 273.15 K and 1.0 atm

Ideal gas at STP = 22.4 L mol^{-1}

THERMODYNAMICS / ELECTROCHEMISTRY

$$q = mc\Delta T$$

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

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

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

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$= -RT \ln K$$
$$= -nFE^\circ$$

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

$$E_{cell} = E_{cell}^\circ - \frac{RT}{nF}\ln Q$$

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)
Q = reaction quotient

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

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

SECTION II BEGINS ON PAGE 6.

CHEMISTRY

Section II

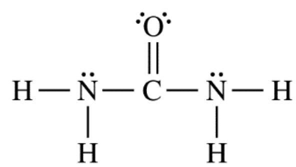
Time—1 hour and 45 minutes

7 Questions

YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.

Directions: Questions 1–3 are long free-response questions that require about 23 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 9 minutes each to answer and are worth 4 points each.

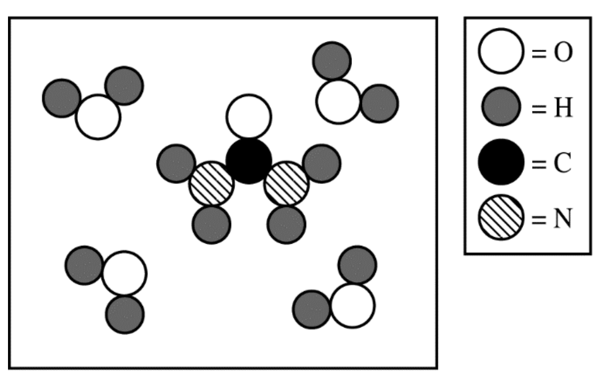
For each question, show your work for each part in the space provided after that part. Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved in arriving at your answers. You must show your work to receive credit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



1. The compound urea, H_2NCONH_2, is widely used in chemical fertilizers. The complete Lewis electron-dot diagram for the urea molecule is shown above.

   (a) Identify the hybridization of the valence orbitals of the carbon atom in the urea molecule.

   (b) Urea has a high solubility in water, due in part to its ability to form hydrogen bonds. A urea molecule and four water molecules are represented in the box below. Draw ONE dashed line (----) to indicate a possible location of a hydrogen bond between a water molecule and the urea molecule.

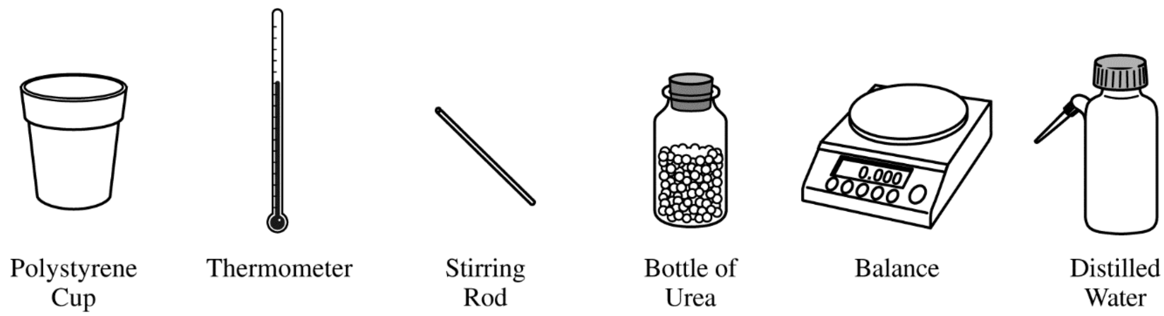


$$H_2NCONH_2(s) \rightleftarrows H_2NCONH_2(aq)$$

The dissolution of urea is represented by the equation above. A student determines that 5.39 grams of H_2NCONH_2 (molar mass 60.06 g/mol) can dissolve in water to make 5.00 mL of a saturated solution at 20.°C.

(c) Calculate the concentration of urea, in mol/L, in the saturated solution at 20.°C.

(d) The student also determines that the concentration of urea in a saturated solution at 25°C is 19.8 *M*. Based on this information, is the dissolution of urea endothermic or exothermic? Justify your answer in terms of Le Chatelier's principle.



(e) The equipment shown above is provided so that the student can determine the value of the molar heat of solution for urea. Knowing that the specific heat of the solution is 4.18 J/(g·°C), list the specific measurements that are required to be made during the experiment.

	$S°$ (J/(mol·K))
$H_2NCONH_2(s)$	104.6
$H_2NCONH_2(aq)$	?

(f) The entropy change for the dissolution of urea, $\Delta S°_{soln}$, is 70.1 J/(mol·K) at 25°C. Using the information in the table above, calculate the absolute molar entropy, $S°$, of aqueous urea.

(g) Using particle-level reasoning, explain why $\Delta S°_{soln}$ is positive for the dissolution of urea in water.

(h) The student claims that $\Delta S°$ for the process contributes to the thermodynamic favorability of the dissolution of urea at 25°C. Use the thermodynamic information above to support the student's claim.

2. Answer the following questions relating to the chemistry of the halogens.

(a) The molecular formulas of diatomic bromine, chlorine, fluorine, and iodine are written below. Circle the formula of the molecule that has the longest bond length. Justify your choice in terms of atomic structure.

Br_2 Cl_2 F_2 I_2

A chemistry teacher wants to prepare Br_2. The teacher has access to the following three reagents: NaBr(*aq*), $Cl_2(g)$, and $I_2(s)$.

Half-Reaction	$E°$ at 25°C (V)
$Br_2 + 2e^- \rightarrow 2Br^-$	1.07
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36
$I_2 + 2e^- \rightarrow 2I^-$	0.53

(b) Using the data in the table above, write the balanced equation for the thermodynamically favorable reaction that will produce Br_2 when the teacher combines two of the reagents. Justify that the reaction is thermodynamically favorable by calculating the value of $E°$ for the reaction.

Br_2 and Cl_2 can react to form the compound $BrCl$.

(c) The boiling point of Br_2 is 332 K, whereas the boiling point of $BrCl$ is 278 K. Explain this difference in boiling point in terms of all the intermolecular forces present between molecules of <u>each</u> substance.

The compound BrCl can decompose into Br_2 and Cl_2, as represented by the balanced chemical equation below.

$$2\ \mathrm{BrCl}(g) \rightleftarrows \mathrm{Br_2}(g) + \mathrm{Cl_2}(g) \qquad \Delta H^\circ = 1.6\ \mathrm{kJ/mol}_{rxn}$$

A 0.100 mole sample of pure BrCl(g) is placed in a previously evacuated, rigid 2.00 L container at 298 K. Eventually the system reaches equilibrium according to the equation above.

(d) Calculate the pressure in the container before equilibrium is established.

(e) Write the expression for the equilibrium constant, K_{eq}, for the decomposition of BrCl.

After the system has reached equilibrium, 42 percent of the original BrCl sample has decomposed.

(f) Determine the value of K_{eq} for the decomposition reaction of BrCl at 298 K.

(g) Calculate the bond energy of the Br-Cl bond, in kJ/mol, using $\Delta H°$ for the reaction (1.6 kJ/mol_{rxn}) and the information in the following table.

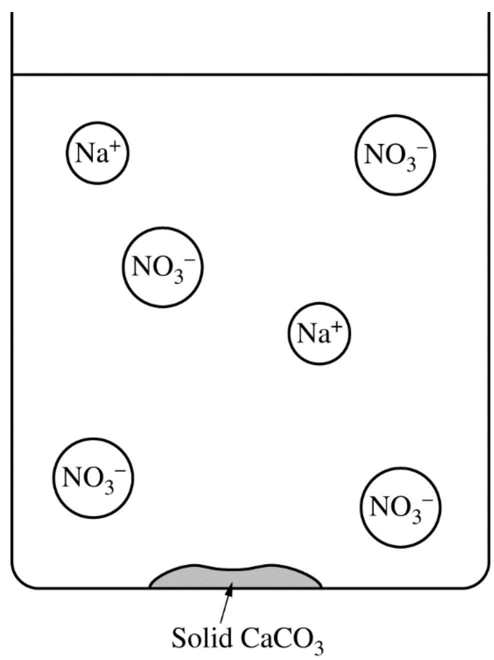
Bond	Bond Energy (kJ/mol)
Br – Br	193
Cl – Cl	243
Br – Cl	?

3. A student is given 50.0 mL of a solution of Na_2CO_3 of unknown concentration. To determine the concentration of the solution, the student mixes the solution with excess 1.0 *M* $Ca(NO_3)_2(aq)$, causing a precipitate to form. The balanced equation for the reaction is shown below.

$$Na_2CO_3(aq) + Ca(NO_3)_2(aq) \rightarrow 2\ NaNO_3(aq) + CaCO_3(s)$$

(a) Write the net ionic equation for the reaction that occurs when the solutions of Na_2CO_3 and $Ca(NO_3)_2$ are mixed.

(b) The diagram below is incomplete. Draw in the species needed to accurately represent the major ionic species remaining in the solution after the reaction has been completed.



The student filters and dries the precipitate of $CaCO_3$ (molar mass 100.1 g/mol) and records the data in the table below.

Volume of Na_2CO_3 solution	50.0 mL
Volume of 1.0 M $Ca(NO_3)_2$ added	100.0 mL
Mass of $CaCO_3$ precipitate collected	0.93 g

(c) Determine the number of moles of Na_2CO_3 in the original 50.0 mL of solution.

(d) The student realizes that the precipitate was not completely dried and claims that as a result, the calculated Na_2CO_3 molarity is too low. Do you agree with the student's claim? Justify your answer.

(e) After the precipitate forms and is filtered, the liquid that passed through the filter is tested to see if it can conduct electricity. What would be observed? Justify your answer.

The student decides to determine the molarity of the same Na_2CO_3 solution using a second method. When Na_2CO_3 is dissolved in water, $CO_3^{2-}(aq)$ hydrolyzes to form $HCO_3^-(aq)$, as shown by the following equation.

$$CO_3^{2-}(aq) + H_2O(l) \rightleftarrows HCO_3^-(aq) + OH^-(aq) \qquad K_b = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = 2.1 \times 10^{-4}$$

(f) The student decides to first determine $[OH^-]$ in the solution, then use that result to calculate the initial concentration of $CO_3^{2-}(aq)$.

(i) Identify a laboratory method (not titration) that the student could use to collect data to determine $[OH^-]$ in the solution.

(ii) Explain how the student could use the measured value in part (f)(i) to calculate the <u>initial</u> concentration of $CO_3^{2-}(aq)$. (Do not do any numerical calculations.)

(g) In the original Na_2CO_3 solution at equilibrium, is the concentration of $HCO_3^-(aq)$ greater than, less than, or equal to the concentration of $CO_3^{2-}(aq)$? Justify your answer.

(h) The student needs to make a CO_3^{2-}/HCO_3^- buffer. Is the Na_2CO_3 solution suitable for making a buffer with a pH of 6 ? Explain why or why not.

4. A student is doing experiments with $CO_2(g)$. Originally, a sample of the gas is in a rigid container at 299 K and 0.70 atm. The student increases the temperature of the $CO_2(g)$ in the container to 425 K.

(a) Describe the effect of raising the temperature on the motion of the $CO_2(g)$ molecules.

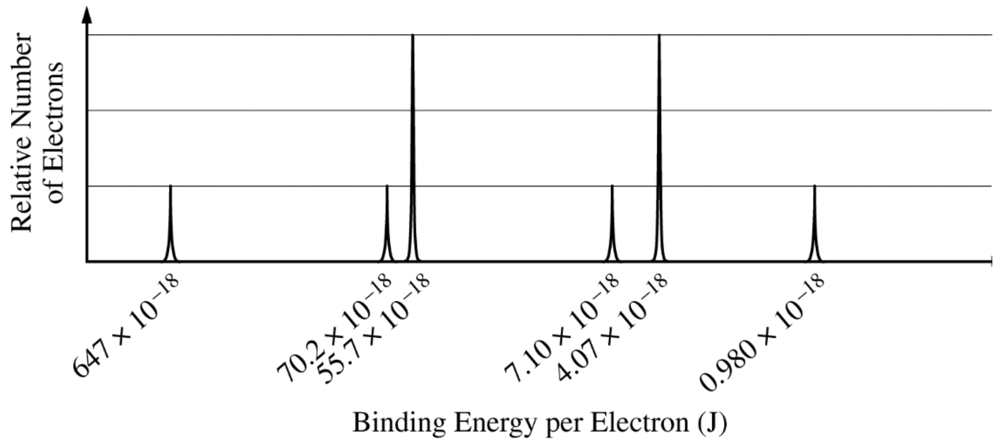
(b) Calculate the pressure of the $CO_2(g)$ in the container at 425 K.

(c) In terms of kinetic molecular theory, briefly explain why the pressure of the $CO_2(g)$ in the container changes as it is heated to 425 K.

GO ON TO THE NEXT PAGE.

(d) The student measures the actual pressure of the $CO_2(g)$ in the container at 425 K and observes that it is less than the pressure predicted by the ideal gas law. Explain this observation.

5. The complete photoelectron spectrum of an element in its ground state is represented below.



(a) Based on the spectrum,

(i) write the ground-state electron configuration of the element, and

(ii) identify the element.

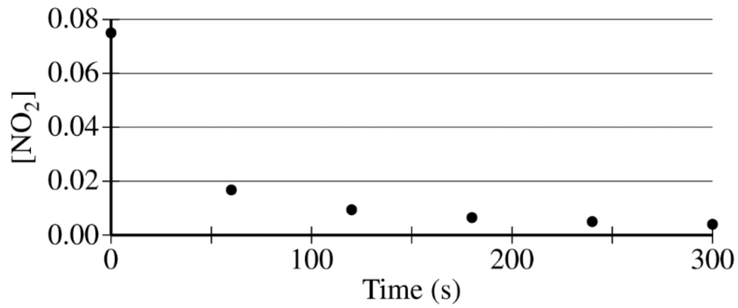
(b) Calculate the wavelength, in meters, of electromagnetic radiation needed to remove an electron from the valence shell of an atom of the element.

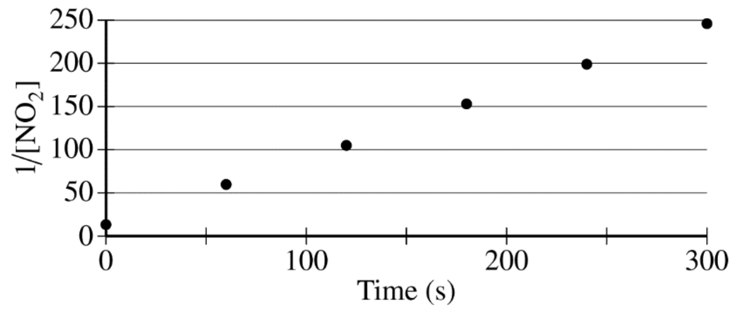
THIS PAGE MAY BE USED FOR SCRATCH WORK FOR THIS QUESTION.

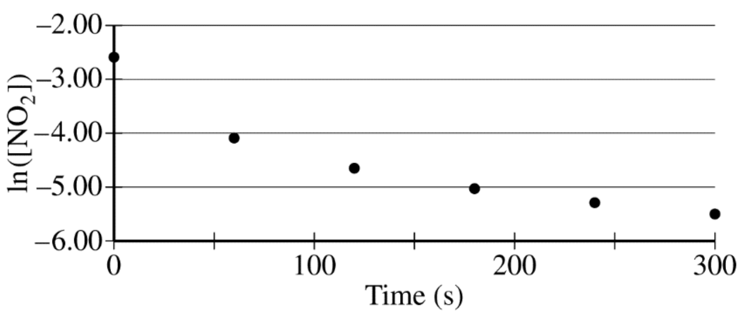
6. Nitrogen dioxide, $NO_2(g)$, is produced as a by-product of the combustion of fossil fuels in internal combustion engines. At elevated temperatures $NO_2(g)$ decomposes according to the equation below.

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

The concentration of a sample of $NO_2(g)$ is monitored as it decomposes and is recorded on the graph directly below. The two graphs that follow it are derived from the original data.







(a) Explain how the graphs indicate that the reaction is second order.

(b) Write the rate law for the decomposition of $NO_2(g)$.

(c) Consider two possible mechanisms for the decomposition reaction.

(i) Is the rate law described by mechanism I shown below consistent with the rate law you wrote in part (b) ? Justify your answer.

Mechanism I

Step 1:	$NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$	*slow*
Step 2:	$NO_3(g) \rightarrow NO(g) + O_2(g)$	*fast*

(ii) Is the rate law described by mechanism II shown below consistent with the rate law you wrote in part (b) ? Justify your answer.

Mechanism II

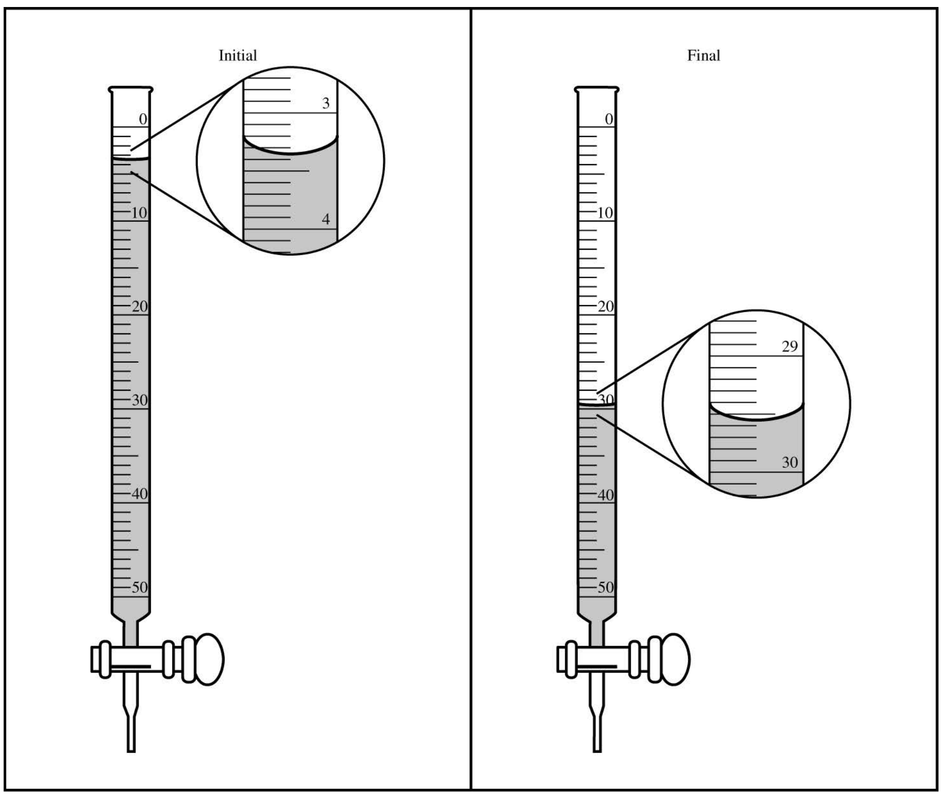
Step 1:	$NO_2(g) + NO_2(g) \rightleftarrows N_2O_4(g)$	*fast equilibrium*
Step 2:	$N_2O_4(g) \rightarrow 2\ NO(g) + O_2(g)$	*slow*

$$6\,H^+(aq) + 2\,MnO_4^-(aq) + 5\,H_2C_2O_4(aq) \rightarrow 10\,CO_2(g) + 8\,H_2O(l) + 2\,Mn^{2+}(aq)$$

7. A student dissolved a 0.139 g sample of oxalic acid, $H_2C_2O_4$, in water in an Erlenmeyer flask. Then the student titrated the $H_2C_2O_4$ solution in the flask with a solution of $KMnO_4$, which has a dark purple color. The balanced chemical equation for the reaction that occurred during the titration is shown above.

   (a) Identify the species that was reduced in the titration reaction. Justify your answer in terms of oxidation numbers.

   (b) The student used a 50.0 mL buret to add the $KMnO_4(aq)$ to the $H_2C_2O_4(aq)$ until a faint lavender color was observed in the flask, an indication that the end point of the titration had been reached. The initial and final volume readings of the solution in the buret are shown below. Write down the initial reading and the final reading and use them to determine the volume of $KMnO_4(aq)$ that was added during the titration.



(c) Given that the concentration of $KMnO_4(aq)$ was 0.0235 M, calculate the number of moles of MnO_4^- ions that completely reacted with the $H_2C_2O_4$.

(d) The student proposes to perform another titration using a 0.139 g sample of $H_2C_2O_4$, but this time using 0.00143 M $KMnO_4(aq)$ in the buret. Would this titrant concentration be a reasonable choice to use if the student followed the same procedure and used the same equipment as before? Justify your response.

STOP

END OF EXAM

IF YOU FINISH BEFORE TIME IS CALLED,
YOU MAY CHECK YOUR WORK ON THIS SECTION.