

AP[®] Chemistry 2004 Free-Response Questions

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INFORMATION IN THE TABLE BELOW AND IN THE TABLES ON PAGES 3-5 MAY BE USEFUL IN ANSWERING THE QUESTIONS IN THIS SECTION OF THE EXAMINATION.

54

83.80

131.29

98

39.948

He 4.0026

.0079

DO NOT DETACH FROM BOOK.

35.453 79.90 126.91 (210)Br 85 At 78.96 (209) 84 208.98 14.007 30.974 74.92 83 Bi Z \$Not yet named PERIODIC TABLE OF THE ELEMENTS 28.09 207.2 18.71 Ge Pb 82 32 50 S 204.38 26.98 10.811 69.72 A 31 81 200.59 12.41 Hg80 ∞ 196.97 107.87 Au 79 195.08 106.42 Z 02.91 192.2 109 Ζt 190.2 108 (265)9/ 54.938 Mn 186.21 Re (86) 75 107 183.85 52.00 95.94 Mo 106 **Sg** (263) 42 > 74 180.95 92.91 S 105 (262)178.49 47.90 (261) 104 H R 227.03 138.91 57 89 137.33 226.02 40.08 87.62 9.012 **Mg** 24.30 20 38 99 88

	58	59	09	61	62	63	64	9	99	29	89	69	70	71
*Lanthanide Series	Ce	Pr	Nd	Pm	Sm	Eu	Сd		Dy	\mathbf{H}_{0}	Er	Tm	Χb	Lu
	140.12	140.91	144.24	(145)	150.4	151.97	157.25		162.50	164.93	167.20	5 168.93	173.04	174.97
	06	91	92	93	94	95	96		86	66	100	101	102	103
Actinide Series	\mathbf{Th}	Pa	n	$N_{\mathbf{p}}$	Pu	Am		Bk	Cf	Es	Fm		No.	Lr
	232.04	231.04	238.03	237.05	(244)	(243)	_	(247)	(251)	(252)		(258)	(259)	(260)

39.10

37

32.91

87

85.47

55

Rb

22.99

19

 \mathbf{Na}

6.941

STANDARD REDUCTION POTENTIALS IN AQUEOUS SOLUTION AT 25° C

	Half-react	ion		$E^{\circ}(V)$
$F_2(g)$ +	2 e-	\rightarrow	2 F ⁻	2.87
2 -		\rightarrow	Co ²⁺	1.82
Au^{3+} +	· 3 e-	\rightarrow	Au(s)	1.50
	+ 2 e ⁻			1.36
$O_2(g)$	$+4 H^{+} + 4 e^{-}$	\rightarrow	$2 H_2O(l)$	1.23
$\operatorname{Br}_2(l)$ -	+ 2 e ⁻	\rightarrow	2 Br-	1.07
2 Hg ²⁺	+ 2 e ⁻	\rightarrow	Hg_{2}^{2+}	0.92
			Hg(l)	0.85
$Ag^+ +$			Ag(s)	0.80
Hg_2^{2+}			2 Hg(<i>l</i>)	0.79
Fe^{3+} +	e^-	\rightarrow	Fe^{2+}	0.77
$I_2(s) +$	2 e-	\rightarrow	2 I ⁻	0.53
Cu ⁺ +	e^-	\rightarrow	Cu(s)	0.52
Cu^{2+} +	2 e-	\rightarrow	Cu(s)	0.34
Cu ²⁺ +	· e-	\rightarrow	Cu ⁺	0.15
Sn ⁴⁺ +	2 e-	\rightarrow	Sn ²⁺	0.15
S(s) + 2	$2 \text{ H}^+ + 2 e^-$	\rightarrow	$H_2S(g)$	0.14
2 H ⁺ +	2 e-	\rightarrow	$H_2(g)$	0.00
		\rightarrow	Pb(s)	-0.13
			Sn(s)	-0.14
			Ni(s)	-0.25
			Co(s)	-0.28
			Tl(s)	
			Cd(s)	
Cr^{3+} +			Cr ²⁺	-0.41
Fe^{2+} +			Fe(s)	-0.44
$Cr^{3+} +$			Cr(s)	-0.74
Zn^{2+} +			Zn(s)	-0.76
Mn^{2+}			Mn(s)	-1.18
$Al^{3+} + P^{2+}$			Al(s)	-1.66
$Be^{2+} +$			Be(s)	
Mg^{2+}			O \ /	-2.37 2.71
Na ⁺ +			Na(s)	-2.71 2.87
$Ca^{2+} + Sr^{2+} +$			Ca(s)	-2.87
Sr^{2+} + Ba^{2+} +			Sr(s)	-2.89 2.00
$Rb^+ +$			Ba(s)	-2.90 2.02
$Kb + K^+ + e$			Rb(s) K(s)	-2.92 -2.92
$Cs^+ + e$			Cs(s)	-2.92 -2.92
$\operatorname{Li}^+ + e$				-2.92 -3.05
$L_1 + e$		\rightarrow	Li(s)	-5.05

ADVANCED PLACEMENT CHEMISTRY EQUATIONS AND CONSTANTS

E = energy

ATOMIC STRUCTURE

$$E = hv c = \lambda v$$

$$\lambda = \frac{h}{mv} p = mv$$

$$E_n = \frac{-2.178 \times 10^{-18}}{n^2} \text{ joule}$$

EQUILIBRIUM

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

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

$$K_{w} = [OH^{-}][H^{+}] = 1.0 \times 10^{-14} @ 25^{\circ}C$$

$$= K_{a} \times K_{b}$$

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

$$14 = pH + pOH$$

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

$$pOH = pK_{b} + \log \frac{[HB^{+}]}{[B]}$$

$$pK_{a} = -\log K_{a}, pK_{b} = -\log K_{b}$$

$$K_{p} = K_{c}(RT)^{\Delta n},$$

where Δn = moles product gas - moles reactant gas

THERMOCHEMISTRY/KINETICS

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

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

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

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

$$= -RT \ln K = -2.303 RT \log K$$

$$= -n \mathcal{F} E^{\circ}$$

$$\Delta G = \Delta G^{\circ} + RT \ln Q = \Delta G^{\circ} + 2.303 RT \log Q$$

$$q = mc\Delta T$$

$$C_{p} = \frac{\Delta H}{\Delta T}$$

$$\ln[A]_{t} - \ln[A]_{0} = -kt$$

$$\frac{1}{[A]_{t}} - \frac{1}{[A]_{0}} = kt$$

$$\ln k = \frac{-E_{a}}{R} \left(\frac{1}{T}\right) + \ln A$$

$$v = \text{frequency}$$
 $n = \text{principal quantum number}$
 $\lambda = \text{wavelength}$ $m = \text{mass}$
 $p = \text{momentum}$
Speed of light, $c = 3.0 \times 10^8 \,\text{m s}^{-1}$
Planck's constant, $h = 6.63 \times 10^{-34} \,\text{J s}$
Boltzmann's constant, $k = 1.38 \times 10^{-23} \,\text{J K}^{-1}$
Avogadro's number $= 6.022 \times 10^{23} \,\text{mol}^{-1}$
Electron charge, $e = -1.602 \times 10^{-19} \,\text{coulomb}$
1 electron volt per atom $= 96.5 \,\text{kJ mol}^{-1}$

v = velocity

Equilibrium Constants

 K_a (weak acid) K_h (weak base) K_{w} (water) K_n (gas pressure)

 K_c (molar concentrations)

 S° = standard entropy H° = standard enthalpy

 G° = standard free energy

 E° = standard reduction potential

T = temperature

n = moles

m = mass

q = heat

c =specific heat capacity

 C_p = molar heat capacity at constant pressure

 E_a = activation energy

k = rate constant

A =frequency factor

Faraday's constant, $\mathcal{F} = 96,500$ coulombs per mole of electrons

Gas constant,
$$R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$$

= 0.0821 L atm mol⁻¹ K⁻¹
= 8.31 volt coulomb mol⁻¹ K⁻¹

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

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

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

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

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

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

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

$$u_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$

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

$$KE \text{ per mole} = \frac{3}{2}RT$$

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\text{molarity, } M = \text{moles solute per liter solution}$$

$$\text{molarity, } M = \text{moles solute per kilogram solvent}$$

$$\Delta T_f = iK_f \times \text{molality}$$

$$\Delta T_b = iK_b \times \text{molality}$$

$$\pi = MRT$$

OXIDATION-REDUCTION; ELECTROCHEMISTRY

A = abc

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

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

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{n\mathcal{F}} \ln Q = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log Q @ 25^\circ \mathbf{C}$$

$$\log K = \frac{nE^\circ}{0.0592}$$

V = volumeT = temperaturen = number of moles D = densitym = massv = velocity u_{rms} = root-mean-square speed KE = kinetic energyr =rate of effusion M = molar mass $\pi = \text{osmotic pressure}$ i = van't Hoff factor K_f = molal freezing-point depression constant K_h = molal boiling-point elevation constant A = absorbancea = molar absorptivityb = path lengthc = concentrationQ = reaction quotientI = current (amperes)q = charge (coulombs)t = time (seconds) E° = standard reduction potential

P = pressure

Gas constant,
$$R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$$

 $= 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$
 $= 8.31 \text{ volt coulomb mol}^{-1} \text{ K}^{-1}$
Boltzmann's constant, $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$
 $K_f \text{ for H}_2\text{O} = 1.86 \text{ K kg mol}^{-1}$
 $K_b \text{ for H}_2\text{O} = 0.512 \text{ K kg mol}^{-1}$
1 atm = 760 mm Hg
= 760 torr
STP = 0.000°C and 1.000 atm

K = equilibrium constant

Faraday's constant, $\mathcal{F} = 96,500$ coulombs per mole of electrons

CHEMISTRY Section II

(Total time—90 minutes)

Part A

Time—40 minutes

YOU MAY USE YOUR CALCULATOR FOR PART A.

CLEARLY SHOW THE METHOD USED AND THE STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, since you may obtain partial credit if you do and you will receive little or no credit if you do not. Attention should be paid to significant figures.

Be sure to write all your answers to the questions on the lined pages following each question in the booklet with the pink cover. Do NOT write your answers on the green insert.

Answer Question 1 below. The Section II score weighting for this question is 20 percent.

1. Answer the following questions relating to the solubilities of two silver compounds, Ag₂CrO₄ and Ag₃PO₄.

Silver chromate dissociates in water according to the equation shown below.

$$Ag_2CrO_4(s) \rightleftharpoons 2 Ag^+(aq) + CrO_4^{2-}(aq)$$
 $K_{sp} = 2.6 \times 10^{-12} \text{ at } 25^{\circ}C$

- (a) Write the equilibrium-constant expression for the dissolving of $Ag_2CrO_4(s)$.
- (b) Calculate the concentration, in mol L^{-1} , of $Ag^{+}(aq)$ in a saturated solution of $Ag_{2}CrO_{4}$ at 25°C.
- (c) Calculate the maximum mass, in grams, of Ag₂CrO₄ that can dissolve in 100. mL of water at 25°C.
- (d) A 0.100 mol sample of solid AgNO₃ is added to a 1.00 L saturated solution of Ag_2CrO_4 . Assuming no volume change, does $[CrO_4^{2-}]$ increase, decrease, or remain the same? Justify your answer.

In a saturated solution of Ag_3PO_4 at 25°C, the concentration of $Ag^+(aq)$ is 5.3×10^{-5} M. The equilibrium-constant expression for the dissolving of $Ag_3PO_4(s)$ in water is shown below.

$$K_{sn} = [Ag^+]^3 [PO_4^{3-}]$$

- (e) Write the balanced equation for the dissolving of Ag₃PO₄ in water.
- (f) Calculate the value of K_{sp} for Ag_3PO_4 at 25°C.
- (g) A 1.00 L sample of saturated Ag₃PO₄ solution is allowed to evaporate at 25°C to a final volume of 500. mL. What is [Ag⁺] in the solution? Justify your answer.

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Answer EITHER Question 2 below OR Question 3 printed on page 8. Only one of these two questions will be graded. If you start both questions, be sure to cross out the question you do not want graded. The Section II score weighting for the question you choose is 20 percent.

$$2 \text{ Fe}(s) + \frac{3}{2} O_2(g) \rightarrow \text{Fe}_2 O_3(s) \qquad \Delta H_f^{\circ} = -824 \text{ kJ mol}^{-1}$$

- 2. Iron reacts with oxygen to produce iron(III) oxide, as represented by the equation above. A 75.0 g sample of Fe(s) is mixed with 11.5 L of $O_2(g)$ at 2.66 atm and 298 K.
 - (a) Calculate the number of moles of each of the following before the reaction begins.
 - (i) Fe(s)
 - (ii) $O_2(g)$
 - (b) Identify the limiting reactant when the mixture is heated to produce $Fe_2O_3(s)$. Support your answer with calculations.
 - (c) Calculate the number of moles of $Fe_2O_3(s)$ produced when the reaction proceeds to completion.
 - (d) The standard free energy of formation, ΔG_f° , of $\mathrm{Fe_2O_3}(s)$ is -740. kJ $\mathrm{mol^{-1}}$ at 298 K.
 - (i) Calculate the standard entropy of formation, ΔS_f° , of Fe₂O₃(s) at 298 K. Include units with your answer.
 - (ii) Which is more responsible for the spontaneity of the formation reaction at 298 K, the standard enthalpy of formation, ΔH_f° , or the standard entropy of formation, ΔS_f° ? Justify your answer.

The reaction represented below also produces iron(III) oxide. The value of ΔH° for the reaction is -280. kJ per mole of Fe₂O₃(s) formed.

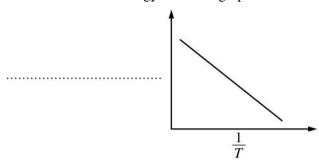
$$2 \operatorname{FeO}(s) + \frac{1}{2} \operatorname{O}_2(g) \to \operatorname{Fe}_2 \operatorname{O}_3(s)$$

(e) Calculate the standard enthalpy of formation, ΔH_f° , of FeO(s).

3. The first-order decomposition of a colored chemical species, X, into colorless products is monitored with a spectrophotometer by measuring changes in absorbance over time. Species X has a molar absorptivity constant of 5.00×10^3 cm⁻¹ M⁻¹ and the path length of the cuvette containing the reaction mixture is 1.00 cm. The data from the experiment are given in the table below.

[X] (M)	Absorbance	Time (min)
?	0.600	0.0
4.00×10^{-5}	0.200	35.0
3.00×10^{-5}	0.150	44.2
1.50×10^{-5}	0.075	?

- (a) Calculate the initial concentration of the colored species.
- (b) Calculate the rate constant for the first-order reaction using the values given for concentration and time. Include units with your answer.
- (c) Calculate the number of minutes it takes for the absorbance to drop from 0.600 to 0.075.
- (d) Calculate the half-life of the reaction. Include units with your answer.
- (e) Experiments were performed to determine the value of the rate constant for this reaction at various temperatures. Data from these experiments were used to produce the graph below, where T is temperature. This graph can be used to determine the activation energy, E_a , of the reaction.
 - (i) Label the vertical axis of the graph.
 - (ii) Explain how to calculate the activation energy from this graph.



STOP

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.

CHEMISTRY

Part B

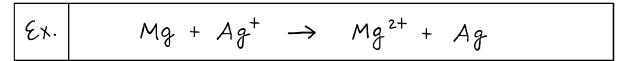
Time—50 minutes

NO CALCULATORS MAY BE USED FOR PART B.

Answer Question 4 below. The Section II score weighting for this question is 15 percent.

4. Write the formulas to show the reactants and the products for any FIVE of the laboratory situations described below. Answers to more than five choices will not be graded. In all cases, a reaction occurs. Assume that solutions are aqueous unless otherwise indicated. Represent substances in solution as ions if the substances are extensively ionized. Omit formulas for any ions or molecules that are unchanged by the reaction. You need not balance the equations.

Example: A strip of magnesium is added to a solution of silver nitrate.



- (a) A solution of copper(II) sulfate is spilled onto a sheet of freshly polished aluminum metal.
- (b) Dimethyl ether is burned in air.
- (c) A 0.1 M nitrous acid solution is added to the same volume of a 0.1 M sodium hydroxide solution.
- (d) Hydrogen iodide gas is bubbled into a solution of lithium carbonate.
- (e) An acidic solution of potassium dichromate is added to a solution of iron(II) nitrate.
- (f) Excess concentrated aqueous ammonia is added to a solution of nickel(II) bromide.
- (g) A solution of sodium phosphate is added to a solution of aluminum nitrate.
- (h) Concentrated hydrochloric acid is added to a solution of sodium sulfide.

Your responses to the rest of the questions in this part of the examination will be graded 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.

Answer BOTH Question 5 below AND Question 6 printed on page 11. Both of these questions will be graded. The Section II score weighting for these questions is 30 percent (15 percent each).

5. In a laboratory class, a student is given three flasks that are labeled Q, R, and S. Each flask contains one of the following solutions: $1.0 M \text{ Pb}(\text{NO}_3)_2$, 1.0 M NaCl, or $1.0 M \text{ K}_2\text{CO}_3$. The student is also given two flasks that are labeled X and Y. One of these flasks contains $1.0 M \text{ AgNO}_3$, and the other contains $1.0 M \text{ BaCl}_2$. This information is summarized in the diagram below.

Each flask contains one of the following solutions:

> Pb(NO₃)₂ NaCl K₂CO₃







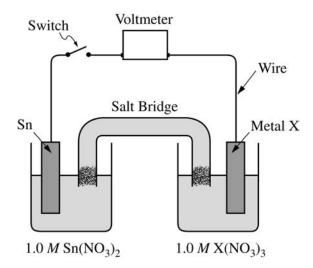
Each flask contains one of the following solutions:

AgNO₃ BaCl₂





- (a) When the student combined a sample of solution Q with a sample of solution X, a precipitate formed. A precipitate also formed when samples of solutions Q and Y were combined.
 - (i) Identify solution Q.
 - (ii) Write the chemical formulas for each of the two precipitates.
- (b) When solution Q is mixed with solution R, a precipitate forms. However, no precipitate forms when solution Q is mixed with solution S.
 - (i) Identify solution R and solution S.
 - (ii) Write the chemical formula of the precipitate that forms when solution Q is mixed with solution R.
- (c) The identity of solution X and solution Y are to be determined using only the following solutions: 1.0 M Pb(NO₃)₂, 1.0 M NaCl, and 1.0 M K₂CO₃.
 - (i) Describe a procedure to identify solution X and solution Y.
 - (ii) Describe the observations that would allow you to distinguish between solution X and solution Y.
 - (iii) Explain how the observations would enable you to distinguish between solution X and solution Y.



6. An electrochemical cell is constructed with an open switch, as shown in the diagram above. A strip of Sn and a strip of an unknown metal, X, are used as electrodes. When the switch is closed, the mass of the Sn electrode increases. The half-reactions are shown below.

$$\operatorname{Sn^{2+}}(aq) + 2 e^{-} \to \operatorname{Sn}(s)$$
 $E^{\circ} = -0.14 \text{ V}$
 $X^{3+}(aq) + 3 e^{-} \to X(s)$ $E^{\circ} = ?$

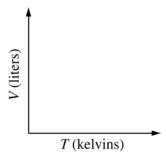
- (a) In the diagram above, label the electrode that is the cathode. Justify your answer.
- (b) In the diagram above, draw an arrow indicating the direction of the electron flow in the external circuit when the switch is closed.
- (c) If the standard cell potential, E_{cell}° , is +0.60 V, what is the standard reduction potential, in volts, for the X^{3+}/X electrode?
- (d) Identify metal X.
- (e) Write a balanced net-ionic equation for the overall chemical reaction occurring in the cell.
- (f) In the cell, the concentration of $\mathrm{Sn^{2+}}$ is changed from 1.0 M to 0.50 M, and the concentration of $\mathrm{X^{3+}}$ is changed from 1.0 M to 0.10 M.
 - (i) Substitute all the appropriate values for determining the cell potential, E_{cell} , into the Nernst equation. (Do <u>not</u> do any calculations.)
 - (ii) On the basis of your response in part (f) (i), will the cell potential, E_{cell} , be greater than, less than, or equal to the original E_{cell}° ? Justify your answer.

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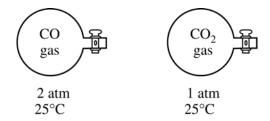
Answer EITHER Question 7 below OR Question 8 printed on page 13. Only one of these two questions will be graded. If you start both questions, be sure to cross out the question you do not want graded. The Section II score weighting for the question you choose is 15 percent.

- 7. Use appropriate chemical principles to account for each of the following observations. In each part, your response <u>must</u> include specific information about <u>both</u> substances.
 - (a) At 25°C and 1 atm, F_2 is a gas, whereas I_2 is a solid.
 - (b) The melting point of NaF is 993°C, whereas the melting point of CsCl is 645°C.
 - (c) The shape of the ICl_4^- ion is square planar, whereas the shape of the BF_4^- ion is tetrahedral.
 - (d) Ammonia, NH₃, is very soluble in water, whereas phosphine, PH₃, is only moderately soluble in water.

- 8. Answer the following questions about carbon monoxide, CO(g), and carbon dioxide, $CO_2(g)$. Assume that both gases exhibit ideal behavior.
 - (a) Draw the complete Lewis structure (electron-dot diagram) for the CO molecule and for the CO₂ molecule.
 - (b) Identify the shape of the CO_2 molecule.
 - (c) One of the two gases dissolves readily in water to form a solution with a pH below 7. Identify the gas and account for this observation by writing a chemical equation.
 - (d) A 1.0 mole sample of CO(g) is heated at constant pressure. On the graph below, sketch the expected plot of volume versus temperature as the gas is heated.



(e) Samples of CO(g) and $CO_2(g)$ are placed in 1 L containers at the conditions indicated in the diagram below.



- (i) Indicate whether the average kinetic energy of the $CO_2(g)$ molecules is greater than, equal to, or less than the average kinetic energy of the CO(g) molecules. Justify your answer.
- (ii) Indicate whether the root-mean-square speed of the $CO_2(g)$ molecules is greater than, equal to, or less than the root-mean-square speed of the CO(g) molecules. Justify your answer.
- (iii) Indicate whether the number of $CO_2(g)$ molecules is greater than, equal to, or less than the number of CO(g) molecules. Justify your answer.

END OF EXAMINATION

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