AP® Chemistry
2002 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.

DO NOT DETACH FROM BOOK.

PERIODIC TABLE OF THE ELEMENTS

1 **H** 1.0079																	2 **He** 4.0026
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.811	6 **C** 12.011	7 **N** 14.007	8 **O** 16.00	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** 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** (263)	107 **Bh** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **§** (269)	111 **§** (272)	112 **§** (277)						

§Not yet named

*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** 237.05	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)

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STANDARD REDUCTION POTENTIALS IN AQUEOUS SOLUTION AT 25°C

Half-reaction			$E°$(V)
$F_2(g) + 2\,e^-$	$\rightarrow$	$2\,F^-$	2.87
$Co^{3+} + e^-$	$\rightarrow$	Co^{2+}	1.82
$Au^{3+} + 3\,e^-$	$\rightarrow$	$Au(s)$	1.50
$Cl_2(g) + 2\,e^-$	$\rightarrow$	$2\,Cl^-$	1.36
$O_2(g) + 4\,H^+ + 4\,e^-$	$\rightarrow$	$2\,H_2O(l)$	1.23
$Br_2(l) + 2\,e^-$	$\rightarrow$	$2\,Br^-$	1.07
$2\,Hg^{2+} + 2\,e^-$	$\rightarrow$	$Hg_2{}^{2+}$	0.92
$Hg^{2+} + 2\,e^-$	$\rightarrow$	$Hg(l)$	0.85
$Ag^+ + e^-$	$\rightarrow$	$Ag(s)$	0.80
$Hg_2{}^{2+} + 2\,e^-$	$\rightarrow$	$2\,Hg(l)$	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
$S(s) + 2\,H^+ + 2\,e^-$	$\rightarrow$	$H_2S(g)$	0.14
$2\,H^+ + 2\,e^-$	$\rightarrow$	$H_2(g)$	0.00
$Pb^{2+} + 2\,e^-$	$\rightarrow$	$Pb(s)$	–0.13
$Sn^{2+} + 2\,e^-$	$\rightarrow$	$Sn(s)$	–0.14
$Ni^{2+} + 2\,e^-$	$\rightarrow$	$Ni(s)$	–0.25
$Co^{2+} + 2\,e^-$	$\rightarrow$	$Co(s)$	–0.28
$Tl^+ + e^-$	$\rightarrow$	$Tl(s)$	–0.34
$Cd^{2+} + 2\,e^-$	$\rightarrow$	$Cd(s)$	–0.40
$Cr^{3+} + e^-$	$\rightarrow$	Cr^{2+}	–0.41
$Fe^{2+} + 2\,e^-$	$\rightarrow$	$Fe(s)$	–0.44
$Cr^{3+} + 3\,e^-$	$\rightarrow$	$Cr(s)$	–0.74
$Zn^{2+} + 2\,e^-$	$\rightarrow$	$Zn(s)$	–0.76
$Mn^{2+} + 2\,e^-$	$\rightarrow$	$Mn(s)$	–1.18
$Al^{3+} + 3\,e^-$	$\rightarrow$	$Al(s)$	–1.66
$Be^{2+} + 2\,e^-$	$\rightarrow$	$Be(s)$	–1.70
$Mg^{2+} + 2\,e^-$	$\rightarrow$	$Mg(s)$	–2.37
$Na^+ + e^-$	$\rightarrow$	$Na(s)$	–2.71
$Ca^{2+} + 2\,e^-$	$\rightarrow$	$Ca(s)$	–2.87
$Sr^{2+} + 2\,e^-$	$\rightarrow$	$Sr(s)$	–2.89
$Ba^{2+} + 2\,e^-$	$\rightarrow$	$Ba(s)$	–2.90
$Rb^+ + e^-$	$\rightarrow$	$Rb(s)$	–2.92
$K^+ + e^-$	$\rightarrow$	$K(s)$	–2.92
$Cs^+ + e^-$	$\rightarrow$	$Cs(s)$	–2.92
$Li^+ + e^-$	$\rightarrow$	$Li(s)$	–3.05

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ATOMIC STRUCTURE

$$\Delta E = h\nu$$
$$c = \lambda\nu$$
$$\lambda = \frac{h}{mv}$$
$$p = mv$$
$$E_n = \frac{-2.178 \times 10^{-18}}{n^2} \text{ joule}$$

E = energy
ν = frequency
λ = wavelength
p = momentum
v = velocity
n = principal quantum number
m = mass

EQUILIBRIUM

$$K_a = \frac{[H^+][A^-]}{[HA]}$$
$$K_b = \frac{[OH^-][HB^+]}{[B]}$$
$$K_w = [OH^-][H^+] = 1.0 \times 10^{-14} \quad @\ 25°C$$
$$= K_a \times K_b$$
$$pH = -\log [H^+],\ pOH = -\log [OH^-]$$
$$14 = pH + pOH$$
$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$
$$pOH = pK_b + \log \frac{[HB^+]}{[B]}$$
$$pK_a = -\log K_a,\ pK_b = -\log K_b$$
$$K_p = K_c(RT)^{\Delta n},$$
where Δn = moles product gas − moles reactant gas

Speed of light, $c = 3.0 \times 10^8 \text{ m s}^{-1}$

Planck's constant, $h = 6.63 \times 10^{-34}$ J s

Boltzmann's constant, $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$

Avogadro's number $= 6.022 \times 10^{23}$ molecules mol^{-1}

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

1 electron volt per atom $= 96.5 \text{ kJ mol}^{-1}$

Equilibrium Constants

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

THERMOCHEMISTRY

$$\Delta S° = \sum S° \text{ products} - \sum S° \text{ reactants}$$
$$\Delta H° = \sum \Delta H_f° \text{ products} - \sum \Delta H_f° \text{ reactants}$$
$$\Delta G° = \sum \Delta G_f° \text{ products} - \sum \Delta G_f° \text{ reactants}$$
$$\Delta G° = \Delta H° - T\Delta S°$$
$$= -RT \ln K = -2.303\, RT \log K$$
$$= -n\mathcal{F}E°$$
$$\Delta G = \Delta G° + RT \ln Q = \Delta G° + 2.303\, RT \log Q$$
$$q = mc\Delta T$$
$$C_p = \frac{\Delta H}{\Delta T}$$

$S°$ = 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
1 faraday $\mathcal{F}$ = 96,500 coulombs

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GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

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

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

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

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

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

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

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

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

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

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

$$\frac{r_1}{r_2} = \sqrt{\frac{\boldsymbol{M}_2}{\boldsymbol{M}_1}}$$

molarity, M = moles solute per liter solution

molality = moles solute per kilogram solvent

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

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

$$\pi = \frac{nRT}{V}i$$

P = pressure
V = volume
T = temperature
n = number of moles
D = density
m = mass
v = velocity

u_{rms} = root-mean-square speed
KE = kinetic energy
r = rate of effusion
$\boldsymbol{M}$ = molar mass
π = osmotic pressure
i = van't Hoff factor
K_f = molal freezing-point depression constant
K_b = molal boiling-point elevation constant
Q = reaction quotient
I = current (amperes)
q = charge (coulombs)
t = time (seconds)
E° = standard reduction potential
K = equilibrium constant

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 for H_2O = $1.86 \text{ K kg mol}^{-1}$

K_b for H_2O = $0.512 \text{ K kg mol}^{-1}$

1 atm = 760 mm Hg
= 760 torr

STP = 0.000°C and 1.000 atm

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

OXIDATION-REDUCTION; ELECTROCHEMISTRY

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

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

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

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

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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.

$$HOBr(aq) \rightleftarrows H^+(aq) + OBr^-(aq) \qquad K_a = 2.3 \times 10^{-9}$$

1. Hypobromous acid, HOBr , is a weak acid that dissociates in water, as represented by the equation above.

   (a) Calculate the value of $[H^+]$ in an HOBr solution that has a pH of 4.95.

   (b) Write the equilibrium constant expression for the ionization of HOBr in water, then calculate the concentration of $HOBr(aq)$ in an HOBr solution that has $[H^+]$ equal to 1.8×10^{-5} *M*.

   (c) A solution of $Ba(OH)_2$ is titrated into a solution of HOBr.

      (i) Calculate the volume of 0.115 *M* $Ba(OH)_2(aq)$ needed to reach the equivalence point when titrated into a 65.0 mL sample of 0.146 *M* $HOBr(aq)$.

      (ii) Indicate whether the pH at the equivalence point is less than 7, equal to 7, or greater than 7. Explain.

   (d) Calculate the number of moles of $NaOBr(s)$ that would have to be added to 125 mL of 0.160 *M* HOBr to produce a buffer solution with $[H^+] = 5.00 \times 10^{-9}$ *M*. Assume that volume change is negligible.

   (e) HOBr is a weaker acid than $HBrO_3$. Account for this fact in terms of molecular structure.

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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. Answer parts (a) through (e) below, which relate to reactions involving silver ion, Ag^+.

The reaction between silver ion and solid zinc is represented by the following equation.

$$2\ Ag^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + 2\ Ag(s)$$

(a) A 1.50 g sample of Zn is combined with 250. mL of 0.110 M $AgNO_3$ at 25°C.

(i) Identify the limiting reactant. Show calculations to support your answer.

(ii) On the basis of the limiting reactant that you identified in part (i), determine the value of $[Zn^{2+}]$ after the reaction is complete. Assume that volume change is negligible.

(b) Determine the value of the standard potential, $E°$, for a galvanic cell based on the reaction between $AgNO_3(aq)$ and solid Zn at 25°C.

Another galvanic cell is based on the reaction between $Ag^+(aq)$ and $Cu(s)$, represented by the equation below. At 25°C, the standard potential, $E°$, for the cell is 0.46 V.

$$2\ Ag^+(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + 2\ Ag(s)$$

(c) Determine the value of the standard free-energy change, $\Delta G°$, for the reaction between $Ag^+(aq)$ and $Cu(s)$ at 25°C.

(d) The cell is constructed so that $[Cu^{2+}]$ is 0.045 M and $[Ag^+]$ is 0.010 M. Calculate the value of the potential, E, for the cell.

(e) Under the conditions specified in part (d), is the reaction in the cell spontaneous? Justify your answer.

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3. Consider the hydrocarbon pentane, C_5H_{12} (molar mass 72.15 g).

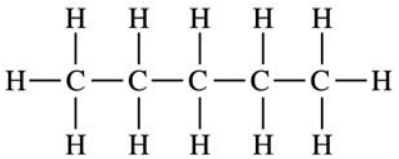
(a) Write the balanced equation for the combustion of pentane to yield carbon dioxide and water.

(b) What volume of dry carbon dioxide, measured at 25°C and 785 mm Hg, will result from the complete combustion of 2.50 g of pentane?

(c) The complete combustion of 5.00 g of pentane releases 243 kJ of heat. On the basis of this information, calculate the value of ΔH for the complete combustion of one mole of pentane.

(d) Under identical conditions, a sample of an unknown gas effuses into a vacuum at twice the rate that a sample of pentane gas effuses. Calculate the molar mass of the unknown gas.

(e) The structural formula of one isomer of pentane is shown below. Draw the structural formulas for the other two isomers of pentane. Be sure to include all atoms of hydrogen and carbon in your structures.



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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.

Ex.	$Mg + Ag^{+} \rightarrow Mg^{2+} + Ag$

   (a) A solution of sodium iodide is added to a solution of lead(II) acetate.

   (b) Pure solid phosphorus (white form) is burned in air.

   (c) Solid cesium oxide is added to water.

   (d) Excess concentrated hydrochloric acid is added to a 1.0 *M* solution of cobalt(II) chloride.

   (e) Solid sodium hydrogen carbonate (sodium bicarbonate) is strongly heated.

   (f) An excess of hydrochloric acid is added to solid zinc sulfide.

   (g) Acidified solutions of potassium permanganate and iron(II) nitrate are mixed together.

   (h) A solution of potassium hydroxide is added to solid ammonium chloride.

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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).

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

5. A student is asked to determine the molar enthalpy of neutralization, ΔH_{neut}, for the reaction represented above. The student combines equal volumes of $1.0\ M$ HCl and $1.0\ M$ NaOH in an open polystyrene cup calorimeter. The heat released by the reaction is determined by using the equation $q = mc\Delta T$.

   Assume the following.

   - Both solutions are at the same temperature before they are combined.
   - The densities of all the solutions are the same as that of water.
   - Any heat lost to the calorimeter or to the air is negligible.
   - The specific heat capacity of the combined solutions is the same as that of water.

   (a) Give appropriate units for each of the terms in the equation $q = mc\Delta T$.

   (b) List the measurements that must be made in order to obtain the value of q.

   (c) Explain how to calculate each of the following.

   (i) The number of moles of water formed during the experiment

   (ii) The value of the molar enthalpy of neutralization, ΔH_{neut}, for the reaction between HCl(aq) and NaOH(aq)

   (d) The student repeats the experiment with the same equal volumes as before, but this time uses $2.0\ M$ HCl and $2.0\ M$ NaOH.

   (i) Indicate whether the value of q increases, decreases, or stays the same when compared to the first experiment. Justify your prediction.

   (ii) Indicate whether the value of the molar enthalpy of neutralization, ΔH_{neut}, increases, decreases, or stays the same when compared to the first experiment. Justify your prediction.

   (e) Suppose that a significant amount of heat were lost to the air during the experiment. What effect would this have on the calculated value of the molar enthalpy of neutralization, ΔH_{neut}? Justify your answer.

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6. Use the principles of atomic structure and/or chemical bonding to explain each of the following. In each part, your answer must include references to both substances.

   (a) The atomic radius of Li is larger than that of Be.

   (b) The second ionization energy of K is greater than the second ionization energy of Ca .

   (c) The carbon-to-carbon bond energy in C_2H_4 is greater than it is in C_2H_6 .

   (d) The boiling point of Cl_2 is lower than the boiling point of Br_2 .

Answer EITHER Question 7 below OR Question 8 printed on page 12. 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. 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 $\quad O_3 + Cl \rightarrow O_2 + ClO$
   Step II $\quad ClO + O \rightarrow Cl + O_2$

   (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

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$$C(s) + CO_2(g) \rightleftarrows 2\,CO(g)$$

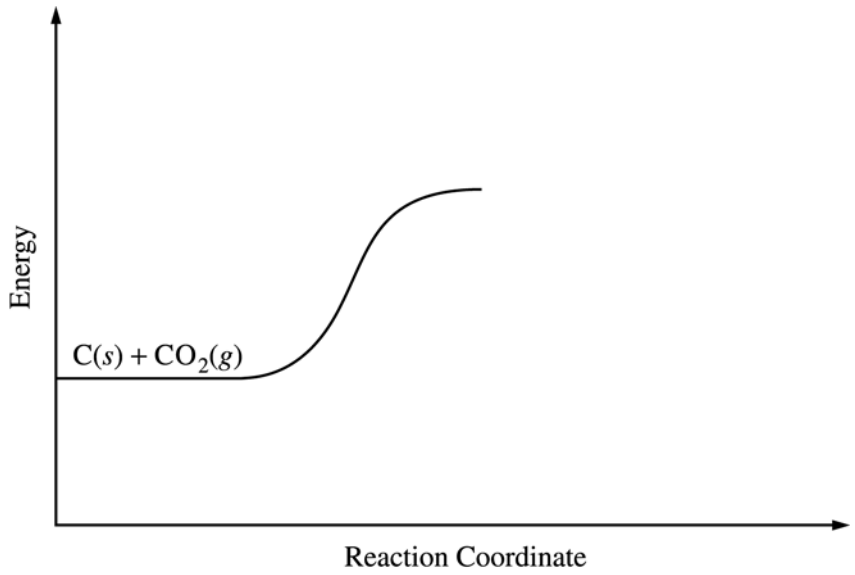
8. Carbon (graphite), carbon dioxide, and carbon monoxide form an equilibrium mixture, as represented by the equation above.

(a) Predict the sign for the change in entropy, ΔS, for the reaction. Justify your prediction.

(b) In the table below are data that show the percent of CO in the equilibrium mixture at two different temperatures. Predict the sign for the change in enthalpy, ΔH, for the reaction. Justify your prediction.

Temperature	% CO
700°C	60
850°C	94

(c) Appropriately complete the potential energy diagram for the reaction by finishing the curve on the graph below. Also, clearly indicate ΔH for the reaction on the graph.



(d) If the initial amount of $C(s)$ were doubled, what would be the effect on the percent of CO in the equilibrium mixture? Justify your answer.

END OF EXAMINATION

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