AP Chemistry
1999 Free-Response Questions

1999

The College Board

Advanced Placement Examination

CHEMISTRY

SECTION II

MATERIAL IN THE FOLLOWING TABLE 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 **Unq** (261)	105 **Unp** (262)	106 **Unh** (263)	107 **Uns** (262)	108 **Uno** (265)	109 **Une** (266)									

*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)

GO ON TO THE NEXT PAGE

1999

STANDARD REDUCTION POTENTIALS IN AQUEOUS SOLUTION AT 25°C

Half-reaction			$E°$(V)
$Li^+ + e^-$	→	$Li(s)$	–3.05
$Cs^+ + e^-$	→	$Cs(s)$	–2.92
$K^+ + e^-$	→	$K(s)$	–2.92
$Rb^+ + e^-$	→	$Rb(s)$	–2.92
$Ba^{2+} + 2e^-$	→	$Ba(s)$	–2.90
$Sr^{2+} + 2e^-$	→	$Sr(s)$	–2.89
$Ca^{2+} + 2e^-$	→	$Ca(s)$	–2.87
$Na^+ + e^-$	→	$Na(s)$	–2.71
$Mg^{2+} + 2e^-$	→	$Mg(s)$	–2.37
$Be^{2+} + 2e^-$	→	$Be(s)$	–1.70
$Al^{3+} + 3e^-$	→	$Al(s)$	–1.66
$Mn^{2+} + 2e^-$	→	$Mn(s)$	–1.18
$Zn^{2+} + 2e^-$	→	$Zn(s)$	–0.76
$Cr^{3+} + 3e^-$	→	$Cr(s)$	–0.74
$Fe^{2+} + 2e^-$	→	$Fe(s)$	–0.44
$Cr^{3+} + e^-$	→	Cr^{2+}	–0.41
$Cd^{2+} + 2e^-$	→	$Cd(s)$	–0.40
$Tl^+ + e^-$	→	$Tl(s)$	–0.34
$Co^{2+} + 2e^-$	→	$Co(s)$	–0.28
$Ni^{2+} + 2e^-$	→	$Ni(s)$	–0.25
$Sn^{2+} + 2e^-$	→	$Sn(s)$	–0.14
$Pb^{2+} + 2e^-$	→	$Pb(s)$	–0.13
$2H^+ + 2e^-$	→	$H_2(g)$	0.00
$S(s) + 2H^+ + 2e^-$	→	$H_2S(g)$	0.14
$Sn^{4+} + 2e^-$	→	Sn^{2+}	0.15
$Cu^{2+} + e^-$	→	Cu^+	0.15
$Cu^{2+} + 2e^-$	→	$Cu(s)$	0.34
$Cu^+ + e^-$	→	$Cu(s)$	0.52
$I_2(s) + 2e^-$	→	$2I^-$	0.53
$Fe^{3+} + e^-$	→	Fe^{2+}	0.77
$Hg_2{}^{2+} + 2e^-$	→	$2Hg(l)$	0.79
$Ag^+ + e^-$	→	$Ag(s)$	0.80
$Hg^{2+} + 2e^-$	→	$Hg(l)$	0.85
$2Hg^{2+} + 2e^-$	→	$Hg_2{}^{2+}$	0.92
$Br_2(l) + 2e^-$	→	$2Br^-$	1.07
$O_2(g) + 4H^+ + 4e^-$	→	$2H_2O(l)$	1.23
$Cl_2(g) + 2e^-$	→	$2Cl^-$	1.36
$Au^{3+} + 3e^-$	→	$Au(s)$	1.50
$Co^{3+} + e^-$	→	Co^{2+}	1.82
$F_2(g) + 2e^-$	→	$2F^-$	2.87

ADVANCED PLACEMENT CHEMISTRY EQUATIONS AND CONSTANTS

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

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

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

Boltzmann's constant, $k = 1.38 \times 10^{-23}$ 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 kJ mol^{-1}

EQUILIBRIUM

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

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

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

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

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

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

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

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

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

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

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

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

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

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

molarity, M = moles solute per liter solution

molality = moles solute per kilogram solvent

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

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

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

OXIDATION-REDUCTION; ELECTROCHEMISTRY

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

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

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

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

P = pressure
V = volume
T = temperature
n = number of moles
D = density
m = mass
υ = 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 J mol^{-1} K^{-1}
= 0.0821 L atm mol^{-1} K^{-1}
= 8.31 volt coulomb mol^{-1} K^{-1}

Boltzmann's constant, k = 1.38×10^{-23} J K^{-1}

K_f for H_2O = 1.86 K kg mol^{-1}

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

STP = 0.000°C and 1.000 atm

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

1999

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 STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, because you may earn 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 this booklet.

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

$$NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$$

1. In aqueous solution, ammonia reacts as represented above. In 0.0180 M $NH_3(aq)$ at 25°C, the hydroxide ion concentration, $[OH^-]$, is 5.60×10^{-4} M. In answering the following, assume that temperature is constant at 25°C and that volumes are additive.

   (a) Write the equilibrium-constant expression for the reaction represented above.

   (b) Determine the pH of 0.0180 M $NH_3(aq)$.

   (c) Determine the value of the base ionization constant, K_b, for $NH_3(aq)$.

   (d) Determine the percent ionization of NH_3 in 0.0180 M $NH_3(aq)$.

   (e) In an experiment, a 20.0 mL sample of 0.0180 M $NH_3(aq)$ was placed in a flask and titrated to the equivalence point and beyond using 0.0120 M $HCl(aq)$.

      (i) Determine the volume of 0.0120 M $HCl(aq)$ that was added to reach the equivalence point.

      (ii) Determine the pH of the solution in the flask after a total of 15.0 mL of 0.0120 M $HCl(aq)$ was added.

      (iii) Determine the pH of the solution in the flask after a total of 40.0 mL of 0.0120 M $HCl(aq)$ was added.

GO ON TO THE NEXT PAGE

Answer EITHER Question 2 below OR Question 3 printed on the next page. 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 the following questions regarding light and its interactions with molecules, atoms, and ions.

(a) The longest wavelength of light with enough energy to break the Cl–Cl bond in $Cl_2(g)$ is 495 nm.

(i) Calculate the frequency, in s^{-1}, of the light.

(ii) Calculate the energy, in J, of a photon of the light.

(iii) Calculate the minimum energy, in kJ mol^{-1}, of the Cl–Cl bond.

(b) A certain line in the spectrum of atomic hydrogen is associated with the electronic transition in the H atom from the sixth energy level ($n = 6$) to the second energy level ($n = 2$).

(i) Indicate whether the H atom emits energy or whether it absorbs energy during the transition. Justify your answer.

(ii) Calculate the wavelength, in nm, of the radiation associated with the spectral line.

(iii) Account for the observation that the amount of energy associated with the same electronic transition ($n = 6$ to $n = 2$) in the He^+ ion is greater than that associated with the corresponding transition in the H atom.

GO ON TO THE NEXT PAGE

$$2\,NO(g) + Br_2(g) \rightarrow 2\,NOBr(g)$$

3. A rate study of the reaction represented above was conducted at 25°C. The data that were obtained are shown in the table below.

Experiment	Initial [NO] (mol L^{-1})	Initial [Br_2] (mol L^{-1})	Initial Rate of Appearance of NOBr (mol L^{-1} s^{-1})
1	0.0160	0.0120	3.24×10^{-4}
2	0.0160	0.0240	6.38×10^{-4}
3	0.0320	0.0060	6.42×10^{-4}

(a) Calculate the initial rate of disappearance of $Br_2(g)$ in experiment 1.

(b) Determine the order of the reaction with respect to each reactant, $Br_2(g)$ and $NO(g)$. In each case, explain your reasoning.

(c) For the reaction,

(i) write the rate law that is consistent with the data, and

(ii) calculate the value of the specific rate constant, k, and specify units.

(d) The following mechanism was proposed for the reaction:

$Br_2(g) + NO(g) \rightarrow NOBr_2(g)$ *slow*

$NOBr_2(g) + NO(g) \rightarrow 2\,NOBr(g)$ *fast*

Is this mechanism consistent with the given experimental observations? Justify your answer.

STOP

DO NOT GO ON TO PART B UNTIL YOU ARE TOLD TO DO SO.

1999

CHEMISTRY

Part B

Time—50 minutes

NO CALCULATORS MAY BE USED WITH 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) Calcium oxide powder is added to distilled water.

(b) Solid ammonium nitrate is heated to temperatures above 300°C.

(c) Liquid bromine is shaken with a 0.5 *M* sodium iodide solution.

(d) Solid lead(II) carbonate is added to a 0.5 *M* sulfuric acid solution.

(e) A mixture of powdered iron(III) oxide and powdered aluminum metal is heated strongly.

(f) Methylamine gas is bubbled into distilled water.

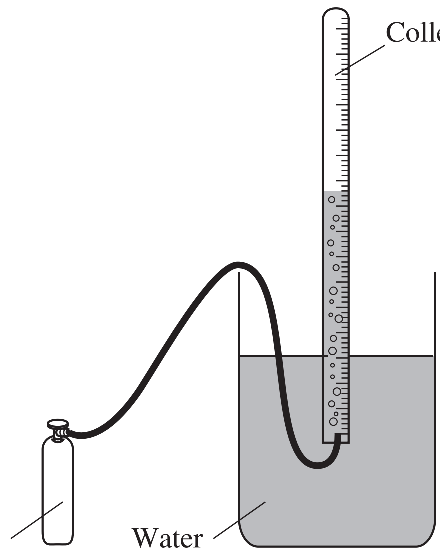
(g) Carbon dioxide gas is passed over hot, solid sodium oxide.

(h) A 0.2 *M* barium nitrate solution is added to an alkaline 0.2 *M* potassium chromate solution.

GO ON TO THE NEXT PAGE

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 the next page. Both of these questions will be graded. The Section II score weighting for these questions is 30 percent (15 percent each).



5. A student performs an experiment to determine the molar mass of an unknown gas. A small amount of the pure gas is released from a pressurized container and collected in a graduated tube over water at room temperature, as shown in the diagram above. The collection tube containing the gas is allowed to stand for several minutes, and its depth is adjusted until the water levels inside and outside the tube are the same. Assume that:

   - the gas is not appreciably soluble in water
   - the gas collected in the graduated tube and the water are in thermal equilibrium
   - a barometer, a thermometer, an analytical balance, and a table of the equilibrium vapor pressure of water at various temperatures are also available.

   (a) Write the equation(s) needed to calculate the molar mass of the gas.

   (b) List the measurements that must be made in order to calculate the molar mass of the gas.

   (c) Explain the purpose of equalizing the water levels inside and outside the gas collection tube.

   (d) The student determines the molar mass of the gas to be 64 g mol^{-1}. Write the expression (set-up) for calculating the percent error in the experimental value, assuming that the unknown gas is butane (molar mass 58 g mol^{-1}). Calculations are not required.

   (e) If the student fails to use information from the table of the equilibrium vapor pressures of water in the calculation, the calculated value for the molar mass of the unknown gas will be smaller than the actual value. Explain.

GO ON TO THE NEXT PAGE

6. Answer the following questions in terms of thermodynamic principles and concepts of kinetic molecular theory.

   (a) Consider the reaction represented below, which is spontaneous at 298 K.

$$CO_2(g) + 2\,NH_3(g) \rightarrow CO(NH_2)_2(s) + H_2O(l) \qquad \Delta H^\circ_{298} = -134 \text{ kJ}$$

   (i) For the reaction, indicate whether the standard entropy change, ΔS°_{298}, is positive, or negative, or zero. Justify your answer.

   (ii) Which factor, the change in enthalpy, ΔH°_{298}, or the change in entropy, ΔS°_{298}, provides the principal driving force for the reaction at 298 K? Explain.

   (iii) For the reaction, how is the value of the standard free energy change, ΔG°, affected by an increase in temperature? Explain.

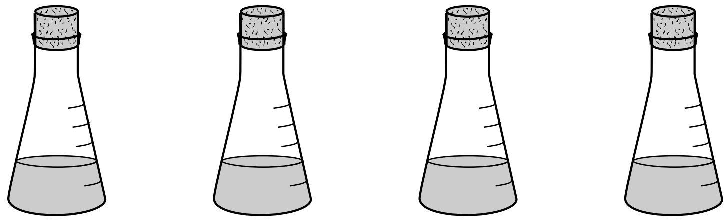
   (b) Some reactions that are predicted by their sign of ΔG° to be spontaneous at room temperature do not proceed at a measurable rate at room temperature.

   (i) Account for this apparent contradiction.

   (ii) A suitable catalyst increases the rate of such a reaction. What effect does the catalyst have on ΔG° for the reaction? Explain.

GO ON TO THE NEXT PAGE

Answer EITHER Question 7 below OR Question 8 below. 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. Answer the following questions, which refer to the 100 mL samples of aqueous solutions at 25°C in the stoppered flasks shown above.

   (a) Which solution has the lowest electrical conductivity? Explain.

   (b) Which solution has the lowest freezing point? Explain.

   (c) Above which solution is the pressure of water vapor greatest? Explain.

   (d) Which solution has the highest pH? Explain.

8. Answer the following questions using principles of chemical bonding and molecular structure.

   (a) Consider the carbon dioxide molecule, CO_2, and the carbonate ion, CO_3^{2-}.

      (i) Draw the complete Lewis electron-dot structure for each species.

      (ii) Account for the fact that the carbon-oxygen bond length in CO_3^{2-} is greater than the carbon-oxygen bond length in CO_2.

   (b) Consider the molecules CF_4 and SF_4.

      (i) Draw the complete Lewis electron-dot structure for each molecule.

      (ii) In terms of molecular geometry, account for the fact that the CF_4 molecule is nonpolar, whereas the SF_4 molecule is polar.

END OF EXAMINATION