

# AP Chemistry 2001 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.

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22.99

19

 $\mathbf{Z}$ 

6.941

71	Lu	174.97		$\operatorname{Lr}$	(260)
70	Ho Er Tm Yb	173.04	102	No	(259)
69	Tm	168.93	101	Md	(258)
89	Er	167.26	100	Fm	(257)
<i>L</i> 9	$\mathbf{H}_0$	164.93	66	Cf Es	(252)
99	Dy	162.50	86	$\mathbf{C}\mathbf{f}$	(251)
65	$\mathbf{T}\mathbf{b}$	158.93	26		_
64		157.25	96	Cm	(247)
63	Eu	151.97	95	Am	(243)
62	Sm		94	Pu	(244)
61	Pm	(145)	93	$\mathbf{N}$	10
09	Nd	40.91 144.24	92	n	238.03
69	Pr	140.91	91	Pa	232.04 231.04
28	Ce	140.12	06	Th	232.04
	*Lanthanide Series			†Actinide Series	

32.91

85.47

55

Rb

37

# STANDARD REDUCTION POTENTIALS IN AQUEOUS SOLUTION AT $25^{\circ}\mathrm{C}$

F	Half-reaction		$E^{\circ}(V)$
$\operatorname{Li}^+ + e^-$	$\rightarrow$	Li(s)	-3.05
$\operatorname{Cs}^+ + e^-$	$\rightarrow$	Cs(s)	-2.92
$K^+ + e^-$	$\rightarrow$	K(s)	-2.92
$Rb^+ + e^-$	$\rightarrow$	Rb(s)	-2.92
$Ba^{2+} + 2e$		Ba(s)	-2.90
$Sr^{2+} + 2e^{-}$		Sr(s)	-2.89
$Ca^{2+} + 2e^{-1}$	?− →	Ca(s)	-2.87
$Na^+ + e^-$	$\rightarrow$	Na(s)	-2.71
$Mg^{2+} + 2$	$e^ \rightarrow$	Mg(s)	-2.37
$Be^{2+} + 2e$	?⁻ →	Be(s)	-1.70
$A1^{3+} + 3e$	_ →	Al(s)	-1.66
$Mn^{2+} + 2$	$e^ \rightarrow$	Mn(s)	-1.18
$Zn^{2+} + 2e$	e⁻ →	Zn(s)	-0.76
$Cr^{3+} + 3e$	$\overline{}$	Cr(s)	-0.74
$Fe^{2+} + 2e$	- →	Fe(s)	-0.44
$Cr^{3+} + e^{-}$	$\rightarrow$	Cr <sup>2+</sup>	-0.41
$Cd^{2+} + 2\epsilon$	e− →	Cd(s)	-0.40
$Tl^+ + e^-$	$\rightarrow$	Tl(s)	-0.34
$Co^{2+} + 2e$	e⁻ →	Co(s)	-0.28
$Ni^{2+} + 2e$	$e^ \rightarrow$	Ni(s)	-0.25
$\operatorname{Sn}^{2+} + 2e$	- →	Sn(s)	-0.14
$Pb^{2+} + 2e$	?⁻ →	Pb(s)	-0.13
$2 H^{+} + 2 e$	?⁻ →	$H_2(g)$	0.00
$S(s) + 2 H^{T}$	$^{+}$ + 2 $e^{-}$ $\rightarrow$	$H_2S(g)$	0.14
$\operatorname{Sn}^{4+} + 2 e$	·- →	$Sn^{2+}$	0.15
$Cu^{2+} + e^{-}$	$\rightarrow$	Cu <sup>+</sup>	0.15
$Cu^{2+} + 2e$	e⁻ →	Cu(s)	0.34
$Cu^+ + e^-$	$\rightarrow$	Cu(s)	0.52
$I_2(s) + 2 e$	$\overline{}$	2 I <sup>-</sup>	0.53
$Fe^{3+} + e^{-}$	$\rightarrow$	Fe <sup>2+</sup>	0.77
$Hg_2^{2+} + 2$	$e^{-}$ $\rightarrow$	2 Hg( <i>l</i> )	0.79
$Ag^+ + e^-$	$\rightarrow$	Ag(s)	0.80
$Hg^{2+} + 2\epsilon$	e− →	Hg(l)	0.85
	$2 e^- \longrightarrow$		
$\operatorname{Br}_2(l) + 2$	$e^ \rightarrow$	2 Br-	1.07
$O_2(g) + 4$	$H^+ + 4 e^- \rightarrow$	$2 H_2O(l)$	1.23
_	$e^ \rightarrow$	_	1.36
	?− →		1.50
	$\rightarrow$		1.82
	e <sup>−</sup> →		
2 (3)			

#### ATOMIC STRUCTURE

$$\Delta E = hv$$

$$c = \lambda v$$

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

$$p = mv$$

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

# **EQUILIBRIUM**

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

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

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

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

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

$$14 = \mathrm{pH} + \mathrm{pOH}$$

$$\mathrm{pH} = \mathrm{p}K_{a} + \log\frac{[\mathrm{A}^{-}]}{[\mathrm{H}\mathrm{A}]}$$

$$\mathrm{pOH} = \mathrm{p}K_{b} + \log\frac{[\mathrm{HB}^{+}]}{[\mathrm{B}]}$$

$$\mathrm{p}K_{a} = -\log K_{a}, \ \mathrm{p}K_{b} = -\log K_{b}$$

$$K_{p} = K_{c}(RT)^{\Delta n},$$
where  $\Delta n$  = moles product gas – moles reactant gas

#### **THERMOCHEMISTRY**

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

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

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

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

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

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

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

$$q = mc\Delta T$$

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

$$E = \text{energy}$$
 $v = \text{frequency}$ 
 $\lambda = \text{wavelength}$ 
 $p = \text{momentum}$ 
 $v = \text{velocity}$ 
 $v = \text{principal quantum number}$ 

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  $= 6.022 \times 10^{23} \text{ molecules mol}^{-1}$   
Electron charge,  $e = -1.602 \times 10^{-19} \text{ coulomb}$   
1 electron volt per atom  $= 96.5 \text{ kJ mol}^{-1}$ 

# **Equilibrium Constants**

Equilibrium Constants
$K_a$ (weak acid)
$K_b$ (weak base)
$K_{w}$ (water)
$K_p$ (gas pressure)
$K_c$ (molar concentrations)

$$S^{\circ} = \operatorname{standard\ entropy}$$
 $H^{\circ} = \operatorname{standard\ enthalpy}$ 
 $G^{\circ} = \operatorname{standard\ free\ energy}$ 
 $E^{\circ} = \operatorname{standard\ reduction\ potential}$ 
 $T = \operatorname{temperature}$ 
 $n = \operatorname{moles}$ 
 $m = \operatorname{mass}$ 
 $q = \operatorname{heat}$ 
 $c = \operatorname{specific\ heat\ capacity}$ 
 $C_p = \operatorname{molar\ heat\ capacity\ at\ constant\ pressure}$ 

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

#### GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

#### OXIDATION-REDUCTION; ELECTROCHEMISTRY

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

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

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

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

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

M = molar mass

 $\pi$  = 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)

 $E^{\circ}$  = standard reduction potential

K = equilibrium constant

Gas constant, 
$$R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$$
  
= 0.0821 L atm mol<sup>-1</sup> K<sup>-1</sup>  
= 8.31 volt coulomb mol<sup>-1</sup> K<sup>-1</sup>

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

$$K_f \text{ for H}_2\text{O} = 1.86 \text{ K kg mol}^{-1}$$

$$K_b \text{ for H}_2\text{O} = 0.512 \text{ K kg mol}^{-1}$$

$$STP = 0.000^{\circ} C$$
 and 1.000 atm

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 solubility of the chlorides of silver and lead.
  - (a) At  $10^{\circ}$ C,  $8.9 \times 10^{-5}$  g of AgCl(s) will dissolve in 100. mL of water.
    - (i) Write the equation for the dissociation of AgCl(s) in water.
    - (ii) Calculate the solubility, in mol  $L^{-1}$ , of AgCl(s) in water at 10°C.
    - (iii) Calculate the value of the solubility-product constant,  $K_{sp}$ , for AgCl(s) at 10°C.
  - (b) At 25°C, the value of  $K_{sp}$  for PbCl<sub>2</sub>(s) is  $1.6 \times 10^{-5}$  and the value of  $K_{sp}$  for AgCl(s) is  $1.8 \times 10^{-10}$ .
    - (i) If 60.0 mL of 0.0400 M NaCl(aq) is added to 60.0 mL of 0.0300 M Pb(NO<sub>3</sub>)<sub>2</sub>(aq), will a precipitate form? Assume that volumes are additive. Show calculations to support your answer.
    - (ii) Calculate the equilibrium value of  $[Pb^{2+}(aq)]$  in 1.00 L of saturated  $PbCl_2$  solution to which 0.250 mole of NaCl(s) has been added. Assume that no volume change occurs.
    - (iii) If  $0.100 \, M$  NaCl(aq) is added slowly to a beaker containing both  $0.120 \, M$  AgNO<sub>3</sub>(aq) and  $0.150 \, M$  Pb(NO<sub>3</sub>)<sub>2</sub>(aq) at 25°C, which will precipitate first, AgCl(s) or PbCl<sub>2</sub>(s)? Show calculations to support your answer.

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.

$$2 \text{ NO}(g) + \text{O}_2(g) \rightarrow 2 \text{ NO}_2(g)$$
  $\Delta H^{\circ} = -114.1 \text{ kJ}, \ \Delta S^{\circ} = -146.5 \text{ J K}^{-1}$ 

- 2. The reaction represented above is one that contributes significantly to the formation of photochemical smog.
  - (a) Calculate the quantity of heat released when 73.1 g of NO(g) is converted to  $NO_2(g)$ .
  - (b) For the reaction at 25°C, the value of the standard free-energy change,  $\Delta G^{\circ}$ , is -70.4 kJ.
    - (i) Calculate the value of the equilibrium constant,  $K_{eq}$ , for the reaction at 25°C.
    - (ii) Indicate whether the value of  $\Delta G^{\circ}$  would become more negative, less negative, or remain unchanged as the temperature is increased. Justify your answer.
  - (c) Use the data in the table below to calculate the value of the standard molar entropy,  $S^{\circ}$ , for  $O_2(g)$  at 25°C.

	Standard Molar Entropy, S° (J K <sup>-1</sup> mol <sup>-1</sup> )
NO(g)	210.8
$NO_2(g)$	240.1

(d) Use the data in the table below to calculate the bond energy, in kJ  $\text{mol}^{-1}$ , of the nitrogen-oxygen bond in  $\text{NO}_2$ . Assume that the bonds in the  $\text{NO}_2$  molecule are equivalent (i.e., they have the same energy).

	Bond Energy (kJ mol <sup>-1</sup> )
Nitrogen-oxygen bond in NO	607
Oxygen-oxygen bond in O <sub>2</sub>	495
Nitrogen-oxygen bond in NO <sub>2</sub>	?

- 3. Answer the following questions about acetylsalicylic acid, the active ingredient in aspirin.
  - (a) The amount of acetylsalicylic acid in a single aspirin tablet is 325 mg, yet the tablet has a mass of 2.00 g. Calculate the mass percent of acetylsalicylic acid in the tablet.
  - (b) The elements contained in acetylsalicylic acid are hydrogen, carbon, and oxygen. The combustion of 3.000 g of the pure compound yields 1.200 g of water and 3.72 L of dry carbon dioxide, measured at 750. mm Hg and 25°C. Calculate the mass, in g, of each element in the 3.000 g sample.
  - (c) A student dissolved 1.625 g of pure acetylsalicylic acid in distilled water and titrated the resulting solution to the equivalence point using 88.43 mL of 0.102 *M* NaOH(*aq*). Assuming that acetylsalicylic acid has only one ionizable hydrogen, calculate the molar mass of the acid.
  - (d) A  $2.00 \times 10^{-3}$  mole sample of pure acetylsalicylic acid was dissolved in 15.00 mL of water and then titrated with  $0.100 \, M$  NaOH(aq). The equivalence point was reached after 20.00 mL of the NaOH solution had been added. Using the data from the titration, shown in the table below, determine
    - (i) the value of the acid dissociation constant,  $K_a$ , for acetylsalicylic acid and
    - (ii) the pH of the solution after a total volume of 25.00 mL of the NaOH solution had been added (assume that volumes are additive).

Volume of 0.100 M NaOH Added (mL)	рН
0.00	2.22
5.00	2.97
10.00	3.44
15.00	3.92
20.00	8.13
25.00	?

#### **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) Sulfur dioxide gas is bubbled into distilled water.
- (b) A drop of potassium thiocyanate solution is added to a solution of iron(III) nitrate.
- (c) A piece of copper wire is placed in a solution of silver nitrate.
- (d) Solutions of potassium hydroxide and propanoic acid are mixed.
- (e) A solution of iron(II) chloride is added to an acidified solution of sodium dichromate.
- (f) Chlorine gas is bubbled through a solution of potassium bromide.
- (g) Solutions of strontium nitrate and sodium sulfate are mixed.
- (h) Powdered magnesium carbonate is heated strongly.

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.

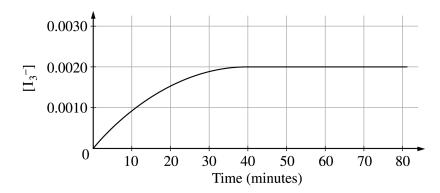
Answer BOTH Question 5 below AND Question 6 printed on page 11. Both of these questions will be graded. The Section II score weighting for these questions is 30 percent (15 percent each).

Solution 1	Solution 2	Solution 3	Solution 4	Solution 5
0.10 M Pb(NO <sub>3</sub> ) <sub>2</sub>	0.10 <i>M</i> NaCl	0.10M KMnO <sub>4</sub>	0.10 <i>M</i> C <sub>2</sub> H <sub>5</sub> OH	$0.10M \\ \mathrm{KC_2H_3O_2}$

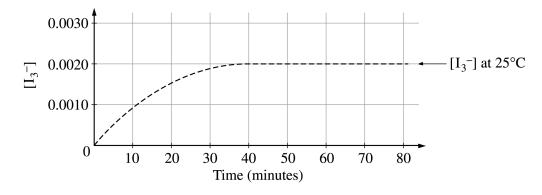
- 5. Answer the questions below that relate to the five aqueous solutions at 25°C shown above.
  - (a) Which solution has the highest boiling point? Explain.
  - (b) Which solution has the highest pH? Explain.
  - (c) Identify a pair of the solutions that would produce a precipitate when mixed together. Write the formula of the precipitate.
  - (d) Which solution could be used to oxidize the  $Cl^{-}(aq)$  ion? Identify the product of the oxidation.
  - (e) Which solution would be the least effective conductor of electricity? Explain.

$$3 I^{-}(aq) + S_2 O_8^{2-}(aq) \rightarrow I_3^{-}(aq) + 2 SO_4^{2-}(aq)$$

- 6. Iodide ion,  $I^-(aq)$ , reacts with peroxydisulfate ion,  $S_2O_8^{2-}(aq)$ , according to the equation above. Assume that the reaction goes to completion.
  - (a) Identify the type of reaction (combustion, disproportionation, neutralization, oxidation-reduction, precipitation, etc.) represented by the equation above. Also, give the formula of another substance that could convert  $I^-(aq)$  to  $I_3^-(aq)$ .
  - (b) In an experiment, equal volumes of  $0.0120 \, M$  I<sup>-</sup>(aq) and  $0.0040 \, M$  S<sub>2</sub>O<sub>8</sub><sup>2-</sup>(aq) are mixed at 25°C. The concentration of I<sub>3</sub><sup>-</sup>(aq) over the following 80 minutes is shown in the graph below.

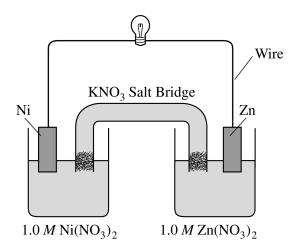


- (i) Indicate the time at which the reaction first reaches completion by marking an "X" on the curve above at the point that corresponds to this time. Explain your reasoning.
- (ii) Explain how to determine the instantaneous rate of formation of  $I_3^-(aq)$  at exactly 20 minutes. Draw on the graph above as part of your explanation.
- (c) Describe how to change the conditions of the experiment in part (b) to determine the order of the reaction with respect to  $I^{-}(aq)$  and with respect to  $S_2O_8^{2-}(aq)$ .
- (d) State clearly how to use the information from the results of the experiments in part (c) to determine the value of the rate constant, *k*, for the reaction.
- (e) On the graph below (which shows the results of the initial experiment as a dashed curve), draw in a curve for the results you would predict if the initial experiment were to be carried out at 35°C rather than at 25°C.



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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. Answer the following questions that refer to the galvanic cell shown in the diagram above. (A table of standard reduction potentials is printed on the green insert and on page 4 of the booklet with the pink cover.)
  - (a) Identify the anode of the cell and write the half-reaction that occurs there.
  - (b) Write the net ionic equation for the overall reaction that occurs as the cell operates and calculate the value of the standard cell potential,  $E_{cell}^{\circ}$ .
  - (c) Indicate how the value of  $E_{cell}$  would be affected if the concentration of Ni(NO<sub>3</sub>)<sub>2</sub>(aq) was changed from 1.0 M to 0.10 M and the concentration of Zn(NO<sub>3</sub>)<sub>2</sub>(aq) remained at 1.0 M. Justify your answer.
  - (d) Specify whether the value of  $K_{eq}$  for the cell reaction is less than 1, greater than 1, or equal to 1. Justify your answer.

- 8. Account for each of the following observations about pairs of substances. In your answers, use appropriate principles of chemical bonding and/or intermolecular forces. In each part, your answer must include references to both substances.
  - (a) Even though  $NH_3$  and  $CH_4$  have similar molecular masses,  $NH_3$  has a much higher normal boiling point  $(-33^{\circ}C)$  than  $CH_4$   $(-164^{\circ}C)$ .
  - (b) At 25°C and 1.0 atm, ethane  $(C_2H_6)$  is a gas and hexane  $(C_6H_{14})$  is a liquid.
  - (c) Si melts at a much higher temperature (1,410°C) than  $\mbox{Cl}_2$  (-101°C).
  - (d) MgO melts at a much higher temperature (2,852°C) than NaF (993°C).

#### **END OF EXAMINATION**