CollegeBoard
Advanced Placement Program

AP® Chemistry
2006 Scoring Guidelines
Form B

Question 1

$$C_6H_5COOH(s) \rightleftarrows C_6H_5COO^-(aq) + H^+(aq) \qquad K_a = 6.46 \times 10^{-5}$$

1. Benzoic acid, C_6H_5COOH, dissociates in water as shown in the equation above. A 25.0 mL sample of an aqueous solution of pure benzoic acid is titrated using standardized 0.150 M NaOH.

(a) After addition of 15.0 mL of the 0.150 M NaOH, the pH of the resulting solution is 4.37. Calculate each of the following.

(i) $[H^+]$ in the solution

$[H^+] = 10^{-4.37}\,M = 4.3 \times 10^{-5}\,M$	One point is earned for the correct answer.

(ii) $[OH^-]$ in the solution

$[OH^-] = \dfrac{K_w}{[H^+]} = \dfrac{1.0 \times 10^{-14}\,M^2}{4.3 \times 10^{-5}\,M} = 2.3 \times 10^{-10}\,M$	One point is earned for the correct answer.

(iii) The number of moles of NaOH added

mol OH^- = $0.0150\text{ L} \times 0.150\text{ mol L}^{-1} = 2.25 \times 10^{-3}$ mol	One point is earned for the correct answer.

(iv) The number of moles of $C_6H_5COO^-(aq)$ in the solution

mol OH^- added = mol $C_6H_5COO^-(aq)$ generated, thus mol $C_6H_5COO^-(aq)$ in solution = 2.25×10^{-3} mol	One point is earned for the correct answer.

(v) The number of moles of C_6H_5COOH in the solution

$K_a = \dfrac{[H^+][C_6H_5COO^-]}{[C_6H_5COOH]} \Rightarrow [C_6H_5COOH] = \dfrac{[H^+][C_6H_5COO^-]}{K_a}$ $[C_6H_5COOH] = \dfrac{(4.3 \times 10^{-5}\,M) \times \dfrac{2.25 \times 10^{-3}\text{ mol}}{0.040\text{ L}}}{6.46 \times 10^{-5}} = 3.7 \times 10^{-2}\,M$ thus, mol C_6H_5COOH = $(0.040\text{ L})(3.7 \times 10^{-2}\,M) = 1.5 \times 10^{-3}$ mol	One point is earned for the correct molarity. One point is earned for the correct answer.

Question 1 (continued)

Alternative solution for part (a)(v):

$\text{pH} = \text{p}K_a + \log \dfrac{[C_6H_5COO^-]}{[C_6H_5COOH]}$ $\Rightarrow \text{pH} - \text{p}K_a = \log [C_6H_5COO^-] - \log [C_6H_5COOH]$ $\Rightarrow \log [C_6H_5COOH] = \log [C_6H_5COO^-] - (\text{pH} - \text{p}K_a)$ $= \log \left(\dfrac{2.25 \times 10^{-3}\text{ mol}}{0.040\text{ L}} \right) - (4.37 - 4.190)$ $= -1.25 - 0.18 = -1.43$ $\Rightarrow [C_6H_5COOH] = 10^{-1.43} = 3.7 \times 10^{-2}\,M$ thus, mol $C_6H_5COOH = (0.040\text{ L})(3.7 \times 10^{-2}\,M) = 1.5 \times 10^{-3}$ mol	

(b) State whether the solution at the equivalence point of the titration is acidic, basic, or neutral. Explain your reasoning.

At the equivalence point the solution is <u>basic</u> due to the presence of $C_6H_5COO^-$ (the conjugate base of the weak acid) that hydrolyzes to produce a basic solution as represented below. $C_6H_5COO^- + H_2O \rightleftarrows C_6H_5COOH + OH^-$	One point is earned for the prediction <u>and</u> the explanation.

In a different titration, a 0.7529 g sample of a mixture of solid C_6H_5COOH and solid NaCl is dissolved in water and titrated with 0.150 M NaOH. The equivalence point is reached when 24.78 mL of the base solution is added.

(c) Calculate each of the following.

(i) The mass, in grams, of benzoic acid in the solid sample

mol $C_6H_5COOH = (0.02478\text{ L}) \times (0.150\text{ mol OH}^-\text{ L}^{-1}) \times \dfrac{1\text{ mol }C_6H_5COOH}{1\text{ mol OH}^-}$ $= 3.72 \times 10^{-3}$ mol C_6H_5COOH mass $C_6H_5COOH = 3.72 \times 10^{-3}$ mol $C_6H_5COOH \times \dfrac{122\text{ g }C_6H_5COOH}{1\text{ mol }C_6H_5COOH}$ $= 0.453$ g C_6H_5COOH	One point is earned for the correct answer.

Question 1 (continued)

(ii) The mass percentage of benzoic acid in the solid sample

mass % $C_6H_5COOH = \frac{0.453\text{ g } C_6H_5COOH}{0.7529\text{ g}} \times 100$ $= 60.2\%$	One point is earned for the correct answer.

Question 2

2. Answer the following questions about voltaic cells.

(a) A voltaic cell is set up using Al/Al^{3+} as one half-cell and Sn/Sn^{2+} as the other half-cell. The half-cells contain equal volumes of solutions and are at standard conditions.

(i) Write the balanced net-ionic equation for the spontaneous cell reaction.

$3\,Sn^{2+} + 2\,Al \rightarrow 3\,Sn + 2\,Al^{3+}$	One point is earned for the correct direction. One point is earned for the balanced net-ionic equation.

(ii) Determine the value, in volts, of the standard potential, $E°$, for the spontaneous cell reaction.

$E° = -0.14\text{ V} - (-1.66\text{ V}) = 1.52\text{ V}$ (or, 1.52 J C^{-1})	One point is earned for the correct answer. (Potential <u>must</u> be positive.)

(iii) Calculate the value of the standard free-energy change, $\Delta G°$, for the spontaneous cell reaction. Include units with your answer.

$\Delta G° = -nFE° = -\frac{6\text{ mol } e^-}{1\text{ mol}} \times \frac{96{,}500\text{ C}}{1\text{ mol } e^-} \times (1.52\text{ J C}^{-1})$ $= -8.80 \times 10^5\text{ J mol}^{-1}$ (or -880 kJ mol^{-1})	One point is earned for indicating the correct mol e^- to mol reaction ratio. One point is earned for the correct answer with correct units.

(iv) If the cell operates until $[Al^{3+}]$ is 1.08 M in the Al/Al^{3+} half-cell, what is $[Sn^{2+}]$ in the Sn/Sn^{2+} half-cell?

change in $[Sn^{2+}] = \frac{0.08\text{ mol } Al^{3+}}{1\text{ L}} \times \frac{3\text{ mol } Sn^{2+}}{2\text{ mol } Al^{3+}} = \frac{0.12\text{ mol } Sn^{2+}}{1\text{ L}}$ $[Sn^{2+}] = 1.00\text{ mol L}^{-1} - 0.12\text{ mol L}^{-1} = 0.88\text{ mol L}^{-1}$	One point is earned for the correct answer.

(b) In another voltaic cell with Al/Al^{3+} and Sn/Sn^{2+} half-cells, $[Sn^{2+}]$ is 0.010 M and $[Al^{3+}]$ is 1.00 M. Calculate the value, in volts, of the cell potential, E_{cell}, at 25°C.

$E_{cell} = 1.52\text{ V} - \frac{0.0592}{6} \log \frac{(1.00)^2}{(0.010)^3}$ $= 1.52\text{ V} - 0.0592\text{ V} = 1.46\text{ V}$	Answers must be consistent with part (a)(i). One point is earned for the proper exponents. One point is earned for the correct substitution of concentrations. One point is earned for the correct answer.

Question 3

3. Answer the following questions about the thermodynamics of the reactions represented below.

Reaction *X*: $\frac{1}{2}I_2(s) + \frac{1}{2}Cl_2(g) \rightleftarrows ICl(g)$ $\Delta H_f^\circ = 18 \text{ kJ mol}^{-1}$, $\Delta S_{298}^\circ = 78 \text{ J K}^{-1}\text{ mol}^{-1}$

Reaction *Y*: $\frac{1}{2}I_2(s) + \frac{1}{2}Br_2(l) \rightleftarrows IBr(g)$ $\Delta H_f^\circ = 41 \text{ kJ mol}^{-1}$, $\Delta S_{298}^\circ = 124 \text{ J K}^{-1}\text{ mol}^{-1}$

(a) Is reaction X, represented above, spontaneous under standard conditions? Justify your answer with a calculation.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $= (18 \text{ kJ mol}^{-1}) - (298 \text{ K})(0.078 \text{ kJ mol}^{-1}\text{ K}^{-1}) = -5 \text{ kJ mol}^{-1}$ Reaction is spontaneous because $\Delta G^\circ < 0$.	One point is earned for the correct value of ΔG°. One point is earned for a correct justification of spontaneity.

(b) Calculate the value of the equilibrium constant, K_{eq}, for reaction X at 25°C.

$\Delta G^\circ = -RT \ln K_{eq} \Rightarrow \ln K_{eq} = -\frac{\Delta G^\circ}{RT}$ $\ln K_{eq} = -\frac{(-5 \text{ kJ mol}^{-1})(10^3 \text{ J kJ}^{-1})}{(8.31 \text{ J mol}^{-1}\text{ K}^{-1})(298 \text{ K})} = 2.019$ $K_{eq} = e^{2.019} = (7.5314) = 8$	One point is earned for the correct answer.

(c) What effect will an increase in temperature have on the equilibrium constant for reaction X? Explain your answer.

$\Delta G^\circ = -RT \ln K_{eq} = \Delta H^\circ - T\Delta S^\circ \Rightarrow \ln K_{eq} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$ Since ΔH° is positive, an increase in T will cause $-\Delta H^\circ/RT$ to become a smaller negative number, therefore K_{eq} will increase. ***OR*** The reaction is endothermic ($\Delta H = +18 \text{ kJ mol}^{-1}$); an increase in temperature shifts the reaction to favor more products relative to the reactants, resulting in an increase in the value of K_{eq}.	One point is earned for the correct choice with a correct explanation.

Question 3 (continued)

(d) Explain why the standard entropy change is greater for reaction Y than for reaction X.

Both reaction X and reaction Y have solid iodine as a reactant, but the second reactant in reaction X is chlorine gas whereas the second reactant in reaction Y is liquid bromine. Liquids have lower entropies than gases, thus in reaction Y the reactants are more ordered (and have lower entropies) than in reaction X. The products of both reaction X and reaction Y have about the same disorder, so the change in entropy from reactants to products is greater in reaction Y than in reaction X.	One point is earned for a correct explanation.

(e) Above what temperature will the value of the equilibrium constant for reaction Y be greater than 1.0 ? Justify your answer with calculations.

$\Delta G° = \Delta H° - T\Delta S°$ $K_{eq} = 1$ when $\Delta G° = 0 \Rightarrow T\Delta S° = \Delta H° \Rightarrow$ $T = \dfrac{\Delta H°}{\Delta S°} = \dfrac{41 \text{ kJ mol}^{-1}}{0.124 \text{ kJ mol}^{-1}\text{K}^{-1}} = 330 \text{ K}$ So when $T > 330$ K, $\Delta G° < 0$ kJ mol^{-1} $\Rightarrow K_{eq} > 1.0$	One point is earned for $\Delta G° = 0$. One point is earned for the correct temperature.

(f) For the vaporization of solid iodine, $I_2(s) \rightarrow I_2(g)$, the value of ΔH°_{298} is 62 kJ mol^{-1}. Using this information, calculate the value of ΔH°_{298} for the reaction represented below.

$$I_2(g) + Cl_2(g) \rightleftarrows 2\,ICl(g)$$

$I_2(s) + Cl_2(g) \rightleftarrows 2\,ICl(g) \quad \Delta H^\circ_{298} = 2 \times 18 \text{ kJ mol}^{-1}$ $I_2(g) \rightleftarrows I_2(s) \quad \Delta H^\circ_{298} = -62 \text{ kJ mol}^{-1}$ ――――――――――――――――― $I_2(g) + Cl_2(g) \rightleftarrows 2\,ICl(g) \quad \Delta H^\circ_{298} = -26 \text{ kJ mol}^{-1}$	One point is earned for ΔH°_{298} of either the first or second equation. One point is earned for the correct sum of the ΔH°_{298} values.

Question 4

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.

General Scoring: Three points can be earned for each reaction: one point for the correct reactant(s) and two points for the correct product(s).

(a) Solid calcium carbonate is strongly heated.

$$CaCO_3 \rightarrow CaO + CO_2$$

(b) A strip of magnesium metal is placed in a solution of iron(II) chloride.

$$Mg + Fe^{2+} \rightarrow Mg^{2+} + Fe$$

(c) Boron trifluoride gas is mixed with ammonia gas.

$$BF_3 + NH_3 \rightarrow F_3BNH_3$$

(d) Excess concentrated hydrochloric acid is added to a solution of nickel(II) nitrate.

$$Ni^{2+} + Cl^- \rightarrow [NiCl_4]^{2-}$$

(e) Solid ammonium chloride is added to a solution of potassium hydroxide.

$$NH_4Cl + OH^- \rightarrow NH_3 + H_2O + Cl^-$$

(f) Propanal is burned in air.

$$CH_3CH_2CHO \text{ (or } C_3H_6O) + O_2 \rightarrow CO_2 + H_2O$$

(g) A strip of aluminum foil is placed in liquid bromine.

$$Al + Br_2 \rightarrow AlBr_3 \text{ (or } Al_2Br_6)$$

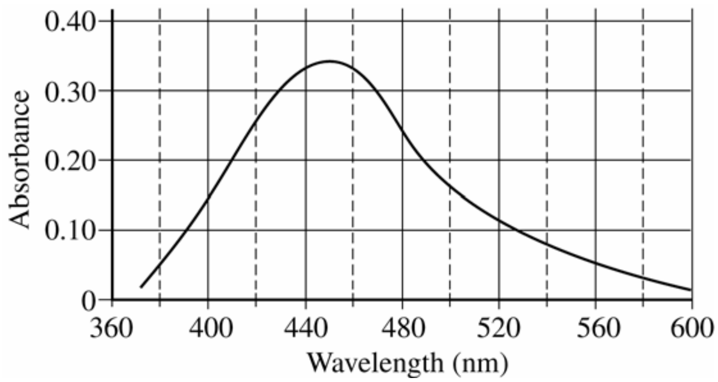
(h) Solid copper(II) sulfide is strongly heated in air.

$$CuS + O_2 \rightarrow CuO + SO_2 \quad \text{(Cu and } SO_3 \text{ are also acceptable as products.)}$$

Question 5

5. A student carries out an experiment to determine the equilibrium constant for a reaction by colorimetric (spectrophotometric) analysis. The production of the red-colored species $FeSCN^{2+}(aq)$ is monitored.

(a) The optimum wavelength for the measurement of $[FeSCN^{2+}]$ must first be determined. The plot of absorbance, A, versus wavelength, λ, for $FeSCN^{2+}(aq)$ is given below. What is the optimum wavelength for this experiment? Justify your answer.



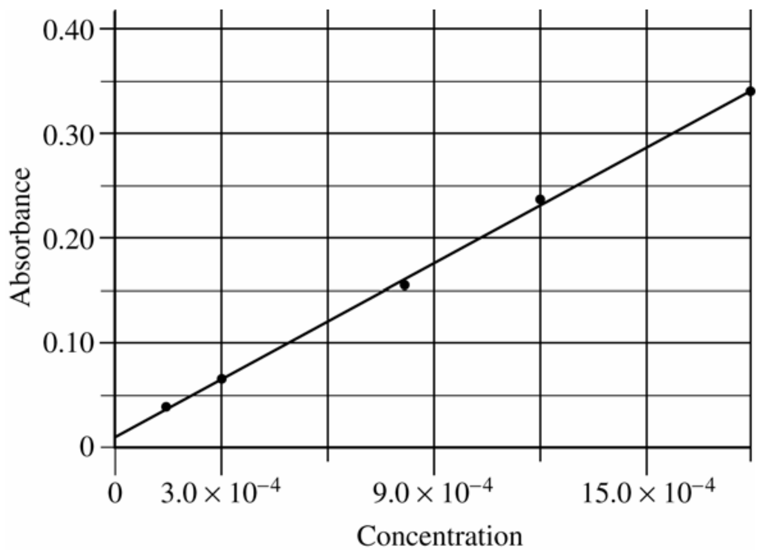
The optimum wavelength is 450 nm <u>because</u> that is the wavelength of maximum absorbance by $FeSCN^{2+}(aq)$.	One point is earned for the correct answer <u>with</u> justification.

(b) A calibration plot for the concentration of $FeSCN^{2+}(aq)$ is prepared at the optimum wavelength. The data below give the absorbances measured for a set of solutions of known concentration of $FeSCN^{2+}(aq)$.

Concentration (mol L^{-1})	Absorbance
1.1×10^{-4}	0.030
3.0×10^{-4}	0.065
8.0×10^{-4}	0.160
12×10^{-4}	0.239
18×10^{-4}	0.340

Question 5 (continued)

(i) Draw a Beer's law calibration plot of all the data on the grid below. Indicate the scale on the horizontal axis by labeling it with appropriate values.



One point is earned for a straight-line plot. One point is earned for a correctly scaled horizontal axis.

(ii) An $FeSCN^{2+}(aq)$ solution of unknown concentration has an absorbance of 0.300. Use the plot you drew in part (i) to determine the concentration, in moles per liter, of this solution.

See plot in part (i). At $A = 0.300$, $[FeSCN^{2+}]$ is approximately 16×10^{-4} mol L^{-1}.	One point is earned for the correct answer.

Question 5 (continued)

(c) The purpose of the experiment is to determine the equilibrium constant for the reaction represented below.

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftarrows FeSCN^{2+}(aq)$$

(i) Write the equilibrium-constant expression for K_c.

$K_c = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^{-}]}$	One point is earned for the correct expression.

(ii) The student combines solutions of $Fe(NO_3)_3$ and KSCN to produce a solution in which the initial concentrations of $Fe^{3+}(aq)$ and $SCN^{-}(aq)$ are both 6.0×10^{-3} M. The absorbance of this solution is measured, and the equilibrium $FeSCN^{2+}(aq)$ concentration is found to be 1.0×10^{-3} M. Determine the value of K_c.

<table><tr><td></td><td>$Fe^{3+}(aq)$</td><td>+</td><td>$SCN^{-}(aq)$</td><td>$\rightleftarrows$</td><td>$FeSCN^{2+}(aq)$</td></tr><tr><td>I</td><td>6.0×10^{-3} M</td><td></td><td>6.0×10^{-3} M</td><td></td><td>0</td></tr><tr><td>C</td><td>-1.0×10^{-3} M</td><td></td><td>-1.0×10^{-3} M</td><td></td><td>$+1.0 \times 10^{-3}$ M</td></tr><tr><td>E</td><td>5.0×10^{-3} M</td><td></td><td>5.0×10^{-3} M</td><td></td><td>$+1.0 \times 10^{-3}$ M</td></tr></table> $K_c = \frac{1.0 \times 10^{-3}}{(5.0 \times 10^{-3})(5.0 \times 10^{-3})} = 40.$	One point is earned for the correct equilibrium concentration. One point is earned for the correct substitutions <u>and</u> the calculated value.

(d) If the student's equilibrium $FeSCN^{2+}(aq)$ solution of unknown concentration fades to a lighter color before the student measures its absorbance, will the calculated value of K_c be too high, too low, or unaffected? Justify your answer.

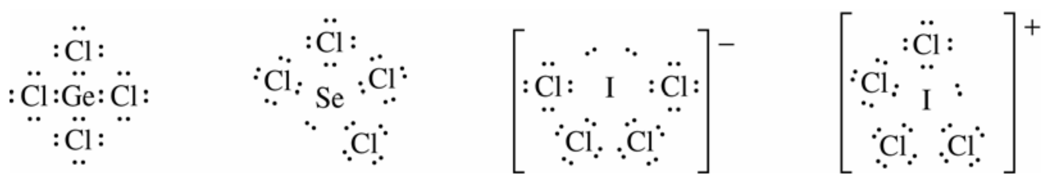
The value of K_c will be too low; the lower absorbance reading indicates a lower $[FeSCN^{2+}]$ than actually existed before the fading occurred, so substitution of a lower $[FeSCN^{2+}]$ into the equilibrium expression will result in a lower value of K_c.	One point is earned for the correct prediction. One point is earned for the correct justification.

Question 6

$GeCl_4$ $SeCl_4$ ICl_4^- ICl_4^+

6. The species represented above all have the same number of chlorine atoms attached to the central atom.

(a) Draw the Lewis structure (electron-dot diagram) of each of the four species. Show all valence electrons in your structures.

	One point is earned for each correct structure.

(b) On the basis of the Lewis structures drawn in part (a), answer the following questions about the particular species indicated.

(i) What is the Cl – Ge – Cl bond angle in $GeCl_4$?

109.5°	One point is earned for the correct angle.

(ii) Is $SeCl_4$ polar? Explain.

Yes. The $SeCl_4$ molecule is polar because the lone pair of nonbonding electrons in the valence shell of the selenium atom interacts with the bonding pairs of electrons, causing a spatial asymmetry of the dipole moments of the polar Se-Cl bonds. The result is a $SeCl_4$ molecule with a net dipole moment.	One point is earned for the correct answer.

(iii) What is the hybridization of the I atom in ICl_4^- ?

d^2sp^3 or sp^3d^2	One point is earned for the correct hybridization.

(iv) What is the geometric shape formed by the atoms in ICl_4^+ ?

See-saw (or distorted tetrahedral or disphenoidal)	One point is earned for the correct shape.

Question 7

7. Account for each of the following observations in terms of atomic theory and/or quantum theory.

(a) Atomic size decreases from Na to Cl in the periodic table.

Across the periodic table from Na to Cl, the number of electrons in the *s*- and *p*- orbitals of the valence shell increases, as does the number of protons in the nucleus. The added electrons only partially shield the added protons, resulting in an increased effective nuclear charge. This results in a greater attraction for the electrons, drawing them closer to the nucleus, making the atom smaller.	One point is earned for indicating the increase in nuclear charge. One point is earned for attributing the size decrease to the greater attraction of the nucleus for the electrons caused by the increase in nuclear charge.

(b) Boron commonly forms molecules of the type BX_3. These molecules have a trigonal planar structure.

Boron has three valence electrons, each of which can form a single covalent bond with X. The three single covalent bonds of the boron atom orient to minimize electron-pair interaction, resulting in bond angles of 120° and a trigonal planar structure.	One point is earned for describing the valence electrons and the bonds. One point is earned for a correct VSEPR argument.

(c) The first ionization energy of K is less than that of Na.

Both Na and K have an s^1 valence-shell electron configuration (Na: [Ne] $3s^1$; K: [Ar] $4s^1$). The K atom valence electron has a higher *n* quantum number, placing it farther from the nucleus than the Na atom valence electron. The greater distance results in less attraction to the nucleus. Because its valence electron is less attracted to its nucleus, the K atom has the lower ionization energy.	One point is earned for the size explanation. One point is earned for describing the attraction to the nucleus.

(d) Each element displays a unique gas-phase emission spectrum.

Each element has a unique set of quantized energy states for its electrons (because of its unique nuclear charge and unique electron configuration). As the electrons of an element absorb quanta of energy, they change to higher energy states (are excited) – during de-excitation, energy is released as EM radiation as the electrons cascade to lower energy states. Each photon of the EM radiation is associated with a specific wavelength ($\lambda = hc/E$), a flux of which produces the lines of the emission spectrum.	One point is earned for describing the quantized energy states and emission phenomenon. One point is earned for describing the effect of the uniqueness of the nucleus and/or electron configuration.

Question 8

8. Use chemical and physical principles to account for each of the following.

(a) An aluminum container filled with an aqueous solution of $CuSO_4$ eventually developed a leak. Include a chemical equation with your answer.

$Al(s) + Cu^{2+}(aq) \rightarrow Al^{3+}(aq) + Cu(s)$ Cu^{2+} has a higher reduction potential than does Al^{3+}, which results in the oxidation and eventual disappearance of the Al metal (depending upon the amount of Cu^{2+}).	One point is earned for the correct equation (phases not required). One point is earned for the explanation of relative reactivity.

(b) The inside of a metal container was cleaned with steam and immediately sealed. Later, the container imploded.

The high temperature of the steam causes the air/water mixture in the container to be at an elevated temperature. When the container is sealed and the temperature decreases, the pressure of the residual gases decreases below the external pressure, causing the implosion. The decrease in pressure occurs because pressure is proportional to temperature and/or vapor pressure of water decrease with temperature, which means that condensation occurs upon cooling with a resultant pressure drop.	One point is earned for explaining the implosion in terms of internal pressure decrease. One point is earned for the explanation of the change of pressure (either cause is accepted).

(c) Skin feels cooler after rubbing alcohol has been applied to it.

Rubbing alcohol evaporates rapidly. Evaporation is endothermic so heat energy is absorbed from the skin in the process, which causes the cooling sensation.	One point is earned for reference to the volatility of the alcohol. One point is earned for discussing the endothermic nature of the process.

(d) The redness and itching of the skin caused by ant bites (injections of methanoic acid, HCO_2H) can be relieved by applying a paste made from water and baking soda (solid sodium hydrogen carbonate). Include a chemical equation with your answer.

$HCO_2H + NaHCO_3 \rightarrow NaHCO_2 + H_2O + CO_2$ Methanoic acid is neutralized by the HCO_3^- ion; with the neutralization of the acid; the redness and itching of the ant bites subside.	One point is earned for the equation. One point is earned for the explanation.