

**STUDENT STUDY GUIDE AND SOLUTIONS
MANUAL FOR ATKINS AND JONES'S**

CHEMICAL PRINCIPLES

THE QUEST FOR INSIGHT

Fifth Edition

**JOHN KRENOS / JOSEPH POTENZA
LAURENCE LAVELLE / YINFA MA / CARL HOEGER**

Student Study Guide and Solutions Manual
for Atkins and Jones's

CHEMICAL PRINCIPLES
The Quest for Insight

Fifth Edition

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SOLUTIONS MANUAL

FUNDAMENTALS

A.1 (a) chemical; (b) physical; (c) physical

A.3 The temperature of the injured camper, the evaporation and condensation of water are physical properties. The ignition of propane is a chemical change.

A.5. (a) Physical; (b) Chemical; (c) Chemical

A.7 (a) intensive; (b) intensive; (c) extensive; (d) extensive

A.9 (a) $1000. \text{ grain} \times \left(\frac{1 \text{ kilograin}}{1,000 \text{ grain}} \right) = 1 \text{ kilograin}$

(b) $0.01 \text{ batman} \times \left(\frac{100 \text{ centibatman}}{1 \text{ batman}} \right) = 1 \text{ centibatman}$

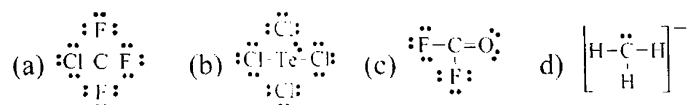
(c) $1 \times 10^6 \text{ mutchkin} \times \left(\frac{1 \text{ megamutchkin}}{10^6 \text{ mutchkin}} \right) = 1 \text{ megamutchkin}$

A.11 $1.00 \text{ cup} \times \left(\frac{1 \text{ pint}}{2 \text{ cups}} \right) \times \left(\frac{1 \text{ quart}}{2 \text{ pints}} \right) \times \left(\frac{0.946 \text{ L}}{1 \text{ quart}} \right) \times \left(\frac{1000 \text{ mL}}{1 \text{ L}} \right) = 236 \text{ mL}$

A.13 $d = \frac{m}{V}$

$$= \left(\frac{112.32 \text{ g}}{29.27 \text{ mL} - 23.45 \text{ mL}} \right) \left(\frac{1 \text{ mL}}{1 \text{ cm}^3} \right)$$
$$= 19.3 \text{ g} \cdot \text{cm}^{-3}$$

3.13 The Lewis structures are



(a) The shape of CF_3Cl is tetrahedral; all halogen—C—halogen angles should be approximately 109.5° . AX_4 ;

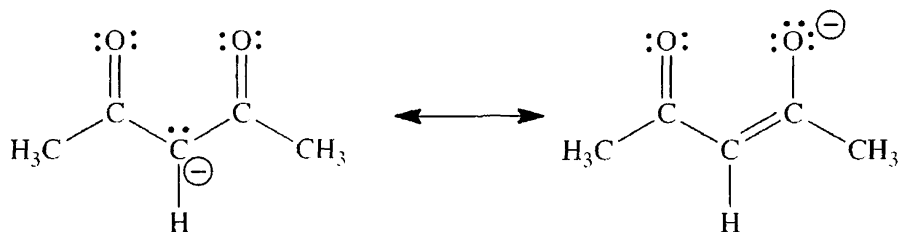
(b) TeCl_4 molecules will be see saw shaped with Cl—Te—Cl bond angles of approximately 90° and 120° . AX_4E ;

(c) COF_2 molecules will be trigonal planar with F—C—F and O—C—F angles of 120° . AX_3 ;

(d) CH_3^- ions will be trigonal pyramidal with H—C—H angles of slightly less than 109.5° . AX_3E

3.15 (a) The angles represented by a and b are expected to be about 120° , while c is expected to be about 109.5° in 2, 4-pentanedione. All of the angles are expected to be about 120° in the acetylacetonate ion.

(b) The major difference arises at the C of the original sp^3 -hybridized CH_2 group, which upon deprotonation and resonance goes to sp^2 hybridization with only three groups attached (the double-headed arrow is read as “in resonance with”):



3.17 (a) slightly less than 120° ; (b) 180° ; (c) 180° ; (d) slightly less than 109.5°

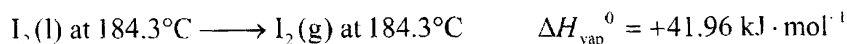
7.95 Appendix 2A provides us with the heat of formation of $I_2(g)$ at 298K ($+62.44 \text{ kJ} \cdot \text{mol}^{-1}$) and the heat capacities of $I_2(g)$ ($36.90 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) and $I_2(s)$ ($54.44 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$). We can calculate the ΔH_{sub}^0 at 298K:



We can calculate the enthalpy of fusion from the relationship

$$\Delta H_{\text{sub}}^0 = \Delta H_{\text{fus}}^0 + \Delta H_{\text{vap}}^0$$

but these values need to be at the same temperature. To correct the value for the fact that we want all the numbers for 298K, we need to alter the heat of vaporization, using the heat capacities for liquid and gaseous iodine.



From Section 6.22, we find the following relationship

$$\Delta H_{T_2}^0 = \Delta H_{T_1}^0 + \Delta C_{P,m}^0 (T_2 - T_1)$$

$$\Delta H_{\text{vap}, 298\text{K}}^0 = \Delta H_{\text{vap}, 475.5\text{K}}^0 + (C_{P,m}^0(I_2, g) - C_{P,m}^0(I_2, l)) (T_2 - T_1)$$

$$\begin{aligned} \Delta H_{\text{vap}, 298\text{K}}^0 &= +41.96 \text{ kJ} \cdot \text{mol}^{-1} \\ &\quad + (36.90 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - 80.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298\text{K} - 475.5\text{K}) \\ &= +49.73 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

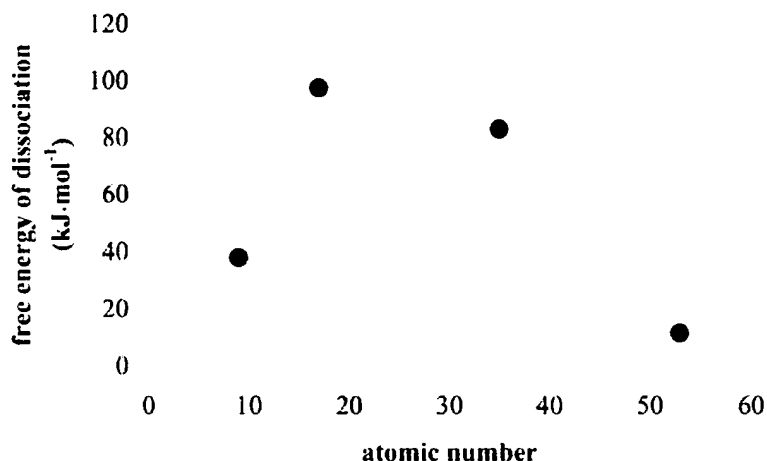
So, at 298K:

$$+62.44 \text{ kJ} \cdot \text{mol}^{-1} = \Delta H_{\text{fus}}^0 + 49.73 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H_{\text{fus}}^0 = +12.71 \text{ kJ} \cdot \text{mol}^{-1}$$

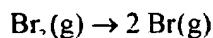
7.97 First, we'll work out how much heat was required to raise the temperature of the water sample: $q = gC\Delta T = (150 \text{ g})(4.18 \text{ J} \cdot ^\circ\text{C}^{-1} \cdot \text{g}^{-1})(5.00^\circ\text{C}) = 3135 \text{ J}$ Since both the water and ice samples were at 0.00°C and the water sample took 0.5 h to get to 5.00°C , we can estimate that the ice took 10.0 h to melt. If 3135 J of heat were transferred in 0.5 h, then the amount of heat transferred in 10.0 h is,

There is a correlation between the bond dissociation energy and the free energy of formation of the atomic species, but the relationship is clearly not linear.



For the heavier three halogens, there is a trend to decreasing free energy of formation of the atoms as the element becomes heavier, but fluorine is anomalous. The F—F bond energy is lower than expected, owing to repulsions of the lone pairs of electrons on the adjacent F atoms because the F—F bond distance is so short.

10.109 (a) Using the thermodynamic data in Appendix 2A:



$$\Delta G^\circ = 2(82.40 \text{ kJ} \cdot \text{mol}^{-1}) - 3.11 \text{ kJ} \cdot \text{mol}^{-1} = 161.69 \text{ kJ} \cdot \text{mol}^{-1}$$

$$K = e^{-\Delta G^\circ / RT} = 4.5 \times 10^{-29}$$

For equilibrium constant calculations, this is reasonably good agreement with the value obtained from part (a), especially if one considers that ΔH° will not be perfectly constant over so large a temperature range.

(b) We will use data from Appendix 2A to calculate the vapor pressure of bromine:

$$(b) \quad E^\circ(\text{Ce}^{4+}/\text{Ce}^{3+}) = +1.61 \text{ V} \quad (\text{anode})$$

$$E^\circ(\text{MnO}_4^-/\text{Mn}^{2+}) = +1.51 \text{ V} \quad (\text{cathode})$$

Because $E^\circ(\text{Ce}^{4+}/\text{Ce}^{3+}) > E^\circ(\text{MnO}_4^-/\text{Mn}^{2+})$, the reaction does not favor products.

$$(c) \quad E^\circ(\text{Pb}^{4+}/\text{Pb}^{2+}) = +1.67 \text{ V} \quad (\text{anode})$$

$$E^\circ(\text{Pb}^{2+}/\text{Pb}) = -0.13 \text{ V} \quad (\text{cathode})$$

Because $E^\circ(\text{Pb}^{4+}/\text{Pb}^{2+}) > E^\circ(\text{Pb}^{2+}/\text{Pb})$, the reaction does not favor products.

$$(d) \quad E^\circ(\text{NO}_3^-/\text{NO}_2/\text{H}^+) = +0.80 \text{ V} \quad (\text{cathode})$$

$$E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V} \quad (\text{anode})$$

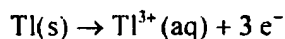
Because $E^\circ(\text{NO}_3^-/\text{NO}_2/\text{H}^+) > E^\circ(\text{Zn}^{2+}/\text{Zn})$, the reaction favors products.

$$E^\circ_{\text{cell}} = +0.80 \text{ V} - (-0.76 \text{ V}) = +1.56 \text{ V}$$

NO_3^- is the oxidizing agent.

13.33 (a) We want E° for $\text{Tl}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Tl}(\text{s})$, $n = 3$.

This reaction is the reverse of the formation reaction:



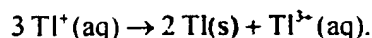
Therefore, for the Tl^{3+}/Tl couple, $\Delta G^\circ_r = -215 \text{ kJ} \cdot \text{mol}^{-1}$.

$$\Delta G^\circ_r = -nFE^\circ = -215 \text{ kJ} \cdot \text{mol}^{-1}$$

$$E^\circ = \frac{\Delta G^\circ_r}{-nF} = \frac{-2.15 \times 10^5 \text{ J} \cdot \text{mol}^{-1}}{-3 \times 9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1}} = +0.743 \text{ V}$$

(b) Using the potential from part (a) and the potential from Appendix 2B

for the reduction of Tl^+ , we can decide whether or not Tl^+ will disproportionate in solution. The equation of interest is



The half-reactions to combine are:

Because we are not given ν , it is easiest to make a relative comparison by taking the ratio of ν for the C—D molecule versus ν for the C—H molecule:

$$\begin{aligned}\frac{\nu_{\text{C-D}}}{\nu_{\text{C-H}}} &= \frac{\frac{1}{2\pi} \sqrt{\frac{k}{\mu_{\text{C-D}}}}}{\frac{1}{2\pi} \sqrt{\frac{k}{\mu_{\text{C-H}}}}} = \sqrt{\frac{\mu_{\text{C-H}}}{\mu_{\text{C-D}}}} = \sqrt{\frac{\frac{m_{\text{C}}m_{\text{H}}}{m_{\text{C}} + m_{\text{H}}}}{\frac{m_{\text{C}}m_{\text{D}}}{m_{\text{C}} + m_{\text{D}}}}} = \sqrt{\frac{(12.011)(1.0078)}{12.011 + 1.0078} \cdot \frac{12.011 + 2.0140}{(12.011)(2.0140)}} \\ &= \sqrt{\frac{(12.105)}{(13.019)}} = 0.73422\end{aligned}$$

We would thus expect the vibrational frequency for the C—D bond to be approximately 0.73 times the value for the C—H bond (lower in energy).

- 17.57** To determine the effective half-life we need to determine the effective rate constant, k_{E} . This constant is equal to the sum of the biological rate constant (k_{B}) and the radioactive decay rate constant (k_{R}), both of which can be obtained from the respective half-lives:

$$\begin{aligned}k_{\text{E}} &= k_{\text{B}} + k_{\text{R}} = \frac{\ln 2}{90.0 \text{ d}} + \frac{\ln 2}{87.4 \text{ d}} = 1.56 \times 10^{-2} \text{ d}^{-1} \\ t_{1/2} (\text{effective}) &= \frac{\ln 2}{1.56 \times 10^{-2} \text{ d}^{-1}} = 44.4 \text{ d}\end{aligned}$$

- 17.59** Remember to convert g to kg.

$$\begin{aligned}\text{(a)} \quad E &= mc^2 = (1.0 \times 10^{-3} \text{ kg})(3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})^2 \\ &= 9.0 \times 10^{13} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} = 9.0 \times 10^{13} \text{ J}\end{aligned}$$

$$\begin{aligned}\text{(b)} \quad E &= mc^2 = (9.109 \times 10^{-31} \text{ kg})(3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})^2 \\ &= 8.20 \times 10^{-14} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} = 8.20 \times 10^{-14} \text{ J}\end{aligned}$$

$$\text{(c)} \quad E = mc^2$$

$$E = (1.0 \times 10^{-15} \text{ kg})(3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})^2 = 90. \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} = 90. \text{ J}$$