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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

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1.103 The ionization energies of the *s*-block metals are considerably lower, thus making it easier for them to lose electrons in chemical reactions.

1.105 (a) metal; (b) nonmetal; (c) metal; (d) metalloid; (e) metalloid; (f) metal

1.107 The peaks observed in the PES spectra correspond to orbital energies; for each energy value seen, a corresponding orbital is present. Thus, if two values are seen in the PES spectrum, that atom has two orbitals (a 1*s* and a 2*s*); one can then use ionization energies to determine the identity of the element. See Figure 1.52 and Appendix 2 for the successive ionization energies of the elements.

(a) The observed values ($7.30\ \text{MJ}\cdot\text{mol}^{-1}$ and $0.52\ \text{MJ}\cdot\text{mol}^{-1}$) correspond respectively to the second ($7300\ \text{kJ}\cdot\text{mol}^{-1}$) and first ($519\ \text{kJ}\cdot\text{mol}^{-1}$) ionization energies of Li ($1s^2 2s^1$).

(b) The PES values observed ($1.6\ \text{MJ}\cdot\text{mol}^{-1}$ and $0.90\ \text{MJ}\cdot\text{mol}^{-1}$) correspond respectively to the second ($1760\ \text{kJ}\cdot\text{mol}^{-1}$) and first ($900\ \text{kJ}\cdot\text{mol}^{-1}$) ionization energies of Be ($1s^2 2s^2$).

1.109 (a) $\dfrac{\nu}{\text{c}} = 3600\ \text{cm}^{-1}$

$\nu = \text{c}(3600\ \text{cm}^{-1})$

$\nu = (2.997\ 92\times10^{8}\ \text{m}\cdot\text{s}^{-1})\ (3600\ \text{cm}^{-1})$

$\nu = (2.997\ 92\times10^{10}\ \text{cm}\cdot\text{s}^{-1})\ (3600\ \text{cm}^{-1})$

$\nu = 1.1\times10^{14}\ \text{s}^{-1}$

(b) From $E = h\nu$: $E = (6.626\ 08\times10^{-34}\ \text{J}\cdot\text{s})(1.079\times10^{14}\ \text{s}^{-1})$

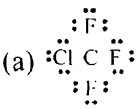
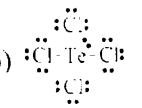
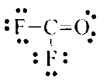
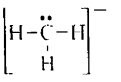
$= 7.2\times10^{-20}\ \text{J}.$

(c) 1.00 mol of molecules $= 6.022\times10^{23}$ molecules, so the energy absorbed by 1.00 mol will be

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3.13 The Lewis structures are

(a)  (b)  (c)  d) 

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

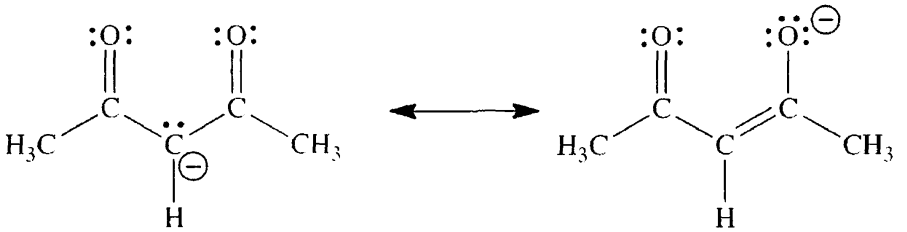
(b) $TeCl_4$ molecules will be see saw shaped with Cl—Te—Cl bond angles of approximately 90° and 120°. AX_4E;

(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 then 109.5°

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5.23 (a) *cis*-Dichloroethene is polar, whereas *trans*-dichloroethene, whose individual bond dipole moments cancel, is nonpolar. Therefore, *cis*-dichloroethene has the greater intermolecular forces and the greater surface tension. (b) Surface tension of liquids decreases with increasing temperature as a result of thermal motion as temperature rises. Increased thermal motion allows the molecules to more easily break away from each other, which manifests itself as decreased surface tension.

5.25 At 50°C all three compounds are liquids. C_6H_6 (nonpolar) < C_6H_5SH (polar, but no hydrogen bonding) < C_6H_5OH (polar and with hydrogen bonding). The viscosity will show the same ordering as the boiling points, which are 80°C for C_6H_6, 169°C for C_6H_5SH, 182° for C_6H_5OH.

5.27 CH_4, -162°C; CH_3CH_3, -88.5°C; $(CH_3)_2CHCH_2CH_3$, 28°C; $CH_3(CH_2)_3CH_3$, 36°C; CH_3OH, 64.5°C; CH_3CH_2OH, 78.3 °C; $CH_3CHOHCH_3$, 82.5°C; C_5H_9OH (cyclic, but not aromatic), 140°C; $C_6H_5CH_3OH$ (aromatic ring), 205°C; $OHCH_2CHOHCH_2OH$, 290°C

5.29 (a) hydrogen bonding; (b) London dispersion forces increase

5.31 Using $h = \dfrac{2\gamma}{gdr}$ we can calculate the height. For water:

$$r = \frac{1}{2}\,diameter = \frac{1}{2}(0.15\text{ mm})\left(\frac{1\text{ m}}{1000\text{ mm}}\right) = 7.5\times10^{-5}\text{ m}$$

$$d = 0.997\text{ g}\cdot\text{cm}^{-3}\left(\frac{1\text{ kg}}{1000\text{ g}}\right)\left(\frac{10^6\text{ cm}^3}{\text{m}^3}\right) = 9.97\times10^{2}\text{ kg}\cdot\text{m}^{-3}$$

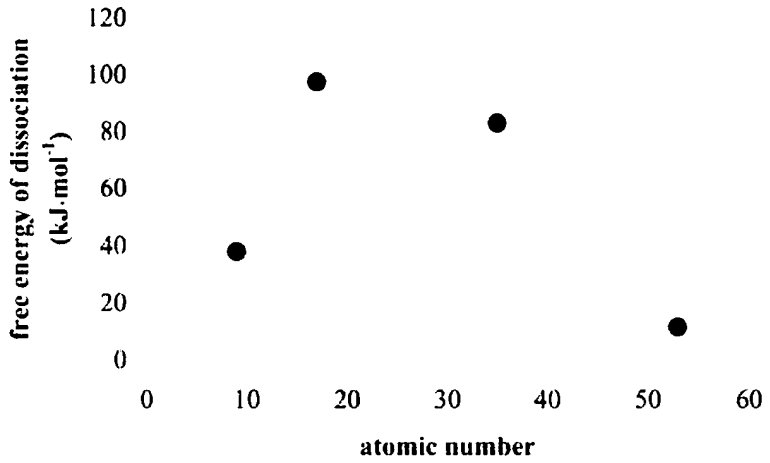
$$h = \frac{2(72.75\times10^{-3}\text{ N}\cdot\text{m}^{-1})}{(9.81\text{ m}\cdot\text{s}^{-1})(9.97\times10^{2}\text{ kg}\cdot\text{m}^{-3})(7.5\times10^{-5}\text{ m})} = 0.20\text{ m or }200\text{ mm}$$

Remember that $1\text{ N} = 1\text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-2}$

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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:

$Br_2(g) \rightarrow 2\ Br(g)$

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

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

For equilibrium constant calculations, this is reasonably good agreement with the value obtained from part (a), especially if one considers that $\Delta H°$ 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:

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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:

$$\frac{\nu_{C\text{-}D}}{\nu_{C\text{-}H}} = \frac{\frac{1}{2\pi}\sqrt{\frac{k}{\mu_{C\text{-}D}}}}{\frac{1}{2\pi}\sqrt{\frac{k}{\mu_{C\text{-}H}}}} = \sqrt{\frac{\mu_{C\text{-}H}}{\mu_{C\text{-}D}}} = \sqrt{\frac{\frac{m_C m_H}{m_C + m_H}}{\frac{m_C m_D}{m_C + m_D}}} = \sqrt{\frac{(12.011)(1.0078)}{12.011 + 1.0078} \over \frac{(12.011)(2.0140)}{12.011 + 2.0140}}$$

$$= \sqrt{\frac{\left(\frac{12.105}{13.019}\right)}{\left(\frac{24.190}{14.025}\right)}} = 0.73422$$

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:

$$k_E = k_B + k_R = \frac{\ln 2}{90.0\ \text{d}} + \frac{\ln 2}{87.4\ \text{d}} = 1.56 \times 10^{-2}\ \text{d}^{-1}$$

$$t_{1/2}\ (\text{effective}) = \frac{\ln 2}{1.56 \times 10^{-2}\ \text{d}^{-1}} = 44.4\ \text{d}$$

17.59 Remember to convert g to kg.

(a) $E = mc^2 = (1.0 \times 10^{-3}\ \text{kg})(3.00 \times 10^{8}\ \text{m} \cdot \text{s}^{-1})^2$

$= 9.0 \times 10^{13}\ \text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2} = 9.0 \times 10^{13}\ \text{J}$

(b) $E = mc^2 = (9.109 \times 10^{-31}\ \text{kg})(3.00 \times 10^{8}\ \text{m} \cdot \text{s}^{-1})^2$

$= 8.20 \times 10^{-14}\ \text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2} = 8.20 \times 10^{-14}\ \text{J}$

(c) $E = mc^2$

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

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