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Problem Solutions

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Solutions

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46 Problem 46

The ratio of the wavelengths of the light absorbed by a Hydrogen atom when it undergoes n=2 → n=3 and n=4 → n=6 transitions, respectively, is

(1) 1/36

(2) 1/16

(3) 1/9

(4) 1/4

Hide Solution

Solution:

Here is a detailed step-by-step solution.

Step 1. Recall the Rydberg formula for hydrogen (absorption or emission) in terms of wavelength:

$$\frac{1}{\lambda} = R_H\Big(\frac{1}{n_{\text{initial}}^2} - \frac{1}{n_{\text{final}}^2}\Big),$$

where R_H is the Rydberg constant.

Step 2. Compute the wavelength for the $n = 2 \to 3$ transition.

Here $n_{\text{initial}} = 2$, $n_{\text{final}} = 3$. Thus

$$\frac{1}{\lambda_{2\to 3}} = R_H\Big(\frac{1}{2^2} - \frac{1}{3^2}\Big) = R_H\Big(\frac{1}{4} - \frac{1}{9}\Big) = R_H\,\frac{9-4}{36} = \frac{5\,R_H}{36},$$

so

$$\lambda_{2\to 3} = \frac{1}{5R_H/36} = \frac{36}{5\,R_H}.$$

Step 3. Compute the wavelength for the $n = 4 \to 6$ transition.

Here $n_{\text{initial}} = 4$, $n_{\text{final}} = 6$. Thus

$$\frac{1}{\lambda_{4\to 6}} = R_H\Big(\frac{1}{4^2} - \frac{1}{6^2}\Big) = R_H\Big(\frac{1}{16} - \frac{1}{36}\Big) = R_H\,\frac{36-16}{576} = \frac{20\,R_H}{576} = \frac{5\,R_H}{144},$$

so

$$\lambda_{4\to 6} = \frac{1}{5R_H/144} = \frac{144}{5\,R_H}.$$

Step 4. Form the ratio of the two wavelengths:

$$\frac{\lambda_{2\to 3}}{\lambda_{4\to 6}} = \frac{\frac{36}{5R_H}}{\frac{144}{5R_H}} = \frac{36}{144} = \frac{1}{4}.$$

Answer: The ratio $\lambda_{2\to3} : \lambda_{4\to6}$ is $\frac{1}{4}$. Hence choice (4).

47 Problem 47

Which of the following statements are true? A. Unlike Ga that has a very high melting point, Cs has a very low melting point. B. On Pauling scale, the electronegativity values of N and Cl are not the same. C. Ar, K^+, Cl^-, Ca^{2+}, and S^{2-} are all isoelectronic species. D. The correct order of the first ionization enthalpies of Na, Mg, Al, and Si is Si > Al > Mg > Na. E. The atomic radius of Cs is greater than that of Li and Rb. Choose the correct answer from the options given below:

(1) A, B, and E only

(2) C and E only

(3) C and D only

(4) A, C, and E only

Hide Solution

Solution:

Here is a statement-by-statement analysis:

1. Statement A
“Unlike Ga that has a very high melting point, Cs has a very low melting point.”

– Actual melting points:

Ga mp = 29.8 °C (very low for a metal),
Cs mp = 28.5 °C (also very low).
– Ga does *not* have a very high melting point – it is liquid just above room temperature.
⇒ A is **false**.

2. Statement B
“On the Pauling scale, the electronegativity values of N and Cl are not the same.”

– More precise Pauling values are

$$\chi_{\mathrm{N}} \approx 3.04, \quad \chi_{\mathrm{Cl}} \approx 3.16.$$

– These are close but definitely *not* identical.
⇒ B is **true**.

3. Statement C
“Ar, K^+, Cl^-, Ca^{2+}, and S^{2-} are all isoelectronic.”

– Number of electrons in each:
- Ar: Z=18 ⇒ 18 e^-
- K^+: Z=19 – 1=18 e^-
- Cl^-: Z=17 + 1=18 e^-
- Ca^{2+}: Z=20 – 2=18 e^-
- S^{2-}: Z=16 + 2=18 e^-

– All have 18 electrons ⇒ isoelectronic.
⇒ C is **true**.

4. Statement D
“The correct order of the first ionization enthalpies of Na, Mg, Al, and Si is

$$\mathrm{Si} > \mathrm{Al} > \mathrm{Mg} > \mathrm{Na}.$$

”

– Experimentally,

$$I_1(\mathrm{Na}) \approx 496\ \mathrm{kJ/mol}, \quad I_1(\mathrm{Mg}) \approx 738\ \mathrm{kJ/mol}, \quad I_1(\mathrm{Al}) \approx 578\ \mathrm{kJ/mol}, \quad I_1(\mathrm{Si})$$

– The correct order is

$$\mathrm{Si} > \mathrm{Mg} > \mathrm{Al} > \mathrm{Na},$$

not Si > Al > Mg > Na.
⇒ D is **false**.

5. Statement E
“The atomic radius of Cs is greater than that of Li and Rb.”

– Atomic radii (approx.):
Li ≈ 152 pm,
Rb ≈ 248 pm,
Cs ≈ 265 pm.
– Clearly Cs > Rb > Li.
⇒ E is **true**.

True statements are B, C and E. However, none of the offered combinations contains exactly B, C and E. If the exam is rounding Pauling electronegativities to one decimal (so that N≈3.0 and Cl≈3.0), then B would be regarded as false and the only remaining true statements would be C and E. In that case the answer is

(2) C and E only.

48 Problem 48

Match List I with List II List-I (Ion): A. Co^{2+} B. Mg^{2+} C. Pb^{2+} D. Al^{3+} List-II (Group Number in Cation Analysis): I. Group-I II. Group-III III. Group-IV IV. Group-VI Choose the correct answer from the options given below:

(1) A-III, B-IV, C-I, D-II

(2) A-III, B-IV, C-I, D-II

A-III, B-II, C-IV, D-I

(3)

(4) A-III, B-II, C-I, D-IV

Hide Solution

Solution:

Here is the step-by-step matching, using the classical six-group scheme of qualitative cation analysis:

1. Recall the four groups we need (from List II):
   I. Group-I (acid-insoluble chlorides, precipitated by HCl)
   II. Group-III (insoluble hydroxides, precipitated by NaOH)
   III. Group-IV (insoluble sulfides in ammoniacal medium, precipitated by $(NH_4)_2S$ + NH_4OH)
   IV. Group-VI (cations remaining in solution after Groups I–V; the "alkali/alkaline-earth" group)

2. Recall which cations fall into each of these four groups:

   - Group-I (with HCl):
     Ag^+, Pb^{2+}, Hg_2^{2+}

   - Group-III (with NaOH):
     Fe^{3+}, Al^{3+}, Cr^{3+} (amphoteric hydroxides)

   - Group-IV (with $(NH_4)_2S$ in NH_4OH):
     Fe^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}

   - Group-VI (remain soluble through Groups I–V):
     Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}

3. Now match each ion from List I to its group:

   A. Co^{2+} $\Longrightarrow$ falls in Group-IV
   $\Rightarrow$ A $\rightarrow$ III

   B. Mg^{2+} $\Longrightarrow$ remains soluble (alkaline-earth) $\rightarrow$ Group-VI
   $\Rightarrow$ B $\rightarrow$ IV

C. $Pb^{2+} \implies$ precipitates as $PbCl_2$ with HCl → Group-I
$\Rightarrow C \rightarrow I$

D. $Al^{3+} \implies$ precipitates as $Al(OH)_3$ with NaOH → Group-III
$\Rightarrow D \rightarrow II$

4. Putting it all together:

A–III, B–IV, C–I, D–II

This corresponds to option **(1)**.

50 Problem 50

Energy and radius of first Bohr orbit of He^+ and Li^{2+} are [Given R_H = 2.18×10^{-18} J ; a_0 = 52.9 pm]

(1) E_n(Li^{2+}) = -19.62×10^{-18} J; r_n(Li^{2+}) = 17.6 pm E_n(He^+) = -8.72×10^{-18} J; r_n(He^+) = 26.4 pm

(2) E_n(Li^{2+}) = -8.72×10^{-18} J; r_n(Li^{2+}) = 26.4 pm E_n(He^+) = -19.62×10^{-18} J; r_n(He^+) = 17.6 pm

(3) E_n(Li^{2+}) = -19.62×10^{-16} J; r_n(Li^{2+}) = 17.6 pm E_n(He^+) = -8.72×10^{-16} J; r_n(He^+) = 26.4 pm

(4) E_n(Li^{2+}) = -8.72×10^{-16} J; r_n(Li^{2+}) = 17.6 pm E_n(He^+) = -19.62×10^{-16} J; r_n(He^+) = 17.6 pm

Hide Solution

Solution:

Step 1: Recall the Bohr-model formulae for an ion of nuclear charge Z in the nth orbit:

Inline energy formula

$$E_n \;=\; -\,\frac{Z^2\,R_H}{n^2}$$

Inline radius formula

$$r_n \;=\; \frac{n^2\,a_0}{Z}$$

Here $R_H = 2.18 \times 10^{-18}\,\mathrm{J}$ and $a_0 = 52.9\,\mathrm{pm}$. We want the first orbit, so set $n = 1$.

Step 2: Compute for He⁺ ($Z = 2$, $n = 1$):

Block energy

$$E_1(\mathrm{He}^+) = -\,\frac{(2)^2\,R_H}{1^2} = -\,4\,R_H = -\,4 \times (2.18 \times 10^{-18}\,\mathrm{J}) = -8.72 \times 10^{-18}\,\mathrm{J}$$

Block radius

$$r_1(\mathrm{He}^+) = \frac{1^2\,a_0}{2} = \frac{52.9\,\mathrm{pm}}{2} = 26.45\,\mathrm{pm} \approx 26.4\,\mathrm{pm}$$

Step 3: Compute for Li²⁺ ($Z = 3$, $n = 1$):

Block energy

$$E_1(\mathrm{Li}^{2+}) = -\frac{(3)^2 R_H}{1^2} = -9\,R_H = -9 \times (2.18 \times 10^{-18}\,\mathrm{J}) = -19.62 \times 10^{-18}\,\mathrm{J}$$

Block radius

$$r_1(\mathrm{Li}^{2+}) = \frac{1^2\,a_0}{3} = \frac{52.9\,\mathrm{pm}}{3} = 17.633\,\mathrm{pm} \approx 17.6\,\mathrm{pm}$$

Step 4: Match with the given options. The values

$$E_1(\mathrm{Li}^{2+}) = -19.62 \times 10^{-18}\,\mathrm{J}, \quad r_1(\mathrm{Li}^{2+}) = 17.6\,\mathrm{pm},$$

$$E_1(\mathrm{He}^{+}) = -8.72 \times 10^{-18}\,\mathrm{J}, \quad r_1(\mathrm{He}^{+}) = 26.4\,\mathrm{pm}$$

correspond exactly to choice **(1)**.

51 Problem 51

Which of the following are paramagnetic? A. $[NiCl_4]^{2-}$ B. $Ni(CO)_4$ C. $[Ni(CN)_4]^{2-}$ D. $[Ni(H_2O)_6]^{2+}$ E. $Ni(PPh_3)_4$ Choose the correct answer from the options given below:

(1) A and C only

(2) B and E only

(3) A and D only

(4) A, D and E only

Hide Solution

Solution:

Here is a full step-by-step analysis. We will for each complex (i) find the Ni oxidation state, (ii) the d-electron count, (iii) the geometry and ligand-field strength, (iv) the d-orbital filling, and (v) the number of unpaired electrons.

1. $[NiCl_4]^{2-}$
   (i) Each Cl^- is –1, so Ni + 4(–1) = –2 ⇒ Ni is +2.
   (ii) Ni^{2+} is d^8.
   (iii) Tetrahedral geometry; Cl^- is a weak-field ligand ⇒ small splitting ($\Delta_t \ll P$, the pairing energy) ⇒ "high-spin."
   (iv) In Td: lower set = e (2 orbitals), upper set = t_2 (3 orbitals). We place 8 electrons:

- Fill e with 4 electrons (2 per orbital).
- Place remaining 4 electrons in t_2 by Hund's rule ⇒ 2 orbitals singly occupied, one orbital doubly occupied.

   (v) There are 2 unpaired electrons ⇒ paramagnetic.

2. $Ni(CO)_4$
   (i) CO is neutral ⇒ Ni oxidation state = 0.
   (ii) Ni^0 is d^{10}.
   (iii) Tetrahedral, but CO is a strong-field ligand ⇒ large splitting, yet all 10 electrons will fill the 5 d orbitals.
   (iv) d^{10} ⇒ every orbital is doubly occupied.
   (v) 0 unpaired electrons ⇒ diamagnetic.

3. $[Ni(CN)_4]^{2-}$
   (i) Each CN^- is –1, so Ni + 4(–1) = –2 ⇒ Ni is +2.
   (ii) Ni^{2+} is d^8.
   (iii) Square-planar geometry; CN^- is a strong-field ligand ⇒ very large splitting ⇒ "low-spin."

(iv) The 8 d electrons fill in order of increasing energy with pairing as needed ⇒ all are paired.
(v) 0 unpaired ⇒ diamagnetic.

4. $[Ni(H_2O)_6]^{2+}$
(i) Each H_2O is neutral ⇒ Ni is +2.
(ii) Ni^{2+} is d^8.
(iii) Octahedral; H_2O is a weak-to-moderate-field ligand ⇒ splitting Δ_o is modest ⇒ "high-spin."
(iv) Fill t_{2g} with 6 electrons, then place 2 electrons in the 2 e_g orbitals singly (Hund's rule).
(v) 2 unpaired electrons ⇒ paramagnetic.

5. $Ni(PPh_3)_4$
(i) PPh_3 is neutral ⇒ Ni is 0.
(ii) Ni^0 is d^{10}.
(iii) Tetrahedral, PPh_3 is a strong donor but d^{10} still fills all orbitals.
(iv) d^{10} ⇒ every orbital is doubly occupied.
(v) 0 unpaired ⇒ diamagnetic.

Summary of unpaired electrons:
A: 2 ⇒ paramagnetic
B: 0 ⇒ diamagnetic
C: 0 ⇒ diamagnetic
D: 2 ⇒ paramagnetic
E: 0 ⇒ diamagnetic

Therefore the only paramagnetic complexes are A and D. That corresponds to choice (3).

52 Problem 52

Given below are two statements : Statement I : Like nitrogen that can form ammonia, arsenic can form arsine. Statement II : Antimony cannot form antimony pentoxide. In the light of the above statements, choose the most appropriate answer from the options given below:

(1) Both Statement I and Statement II are correct

(2) Both Statement I and Statement II are incorrect

(3) Statement I is correct but Statement II is incorrect

(4) Statement I is incorrect but Statement II is correct

Hide Solution

Solution:

Here is a detailed, step-by-step analysis.

Step 1: Recall the hydrides of Group 15 (pnictogens)
Elements in Group 15 (N, P, As, Sb, Bi) form trihydrides of the general formula MH_3:

$$\begin{aligned} \mathrm{N} &\longrightarrow \mathrm{NH_3} \quad (\text{ammonia}), \\ \mathrm{P} &\longrightarrow \mathrm{PH_3} \quad (\text{phosphine}), \\ \mathrm{As} &\longrightarrow \mathrm{AsH_3} \quad (\text{arsine}), \\ \mathrm{Sb} &\longrightarrow \mathrm{SbH_3} \quad (\text{stibine}), \\ \mathrm{Bi} &\longrightarrow \mathrm{BiH_3} \quad (\text{bismuthine}). \end{aligned}$$

– In particular, arsenic does indeed form AsH_3 (arsine).
→ Statement I (“Like nitrogen that can form ammonia, arsenic can form arsine.”) is **correct**.

Step 2: Oxidation states and oxides of antimony
Antimony (Sb) commonly exhibits the +3 and +5 oxidation states. Its two well-known oxides are:

$$\begin{aligned} &\mathrm{Sb_2O_3} \quad (\text{antimony(III) oxide}), \\ &\mathrm{Sb_2O_5} \quad (\text{antimony(V) oxide, “antimony pentoxide”}). \end{aligned}$$

Antimony pentoxide, Sb_2O_5, is a real compound (though it tends to dehydrate at higher temperatures).

– Therefore the claim “Antimony cannot form antimony pentoxide” is **false**.
→ Statement II is **incorrect**.

Step 3: Choose the correct option
- Statement I is correct.
- Statement II is incorrect.

Hence the answer is option **(3)**:
“Statement I is correct but Statement II is incorrect.”

53 Problem 53

Which among the following electronic configurations belong to main group elements? A. [Ne] $3s^1$ B. [Ar] $3d^3\ 4s^2$ C. [Kr] $4d^{10}\ 5s^2\ 5p^5$ D. [Ar] $3d^{10}\ 4s^1$ E. [Rn] $5f^0\ 6d^2\ 7s^2$ Choose the correct answer from the option given below:

(1) B and E only

(2) A and C only

(3) D and E only

(4) A, C and D only

Hide Solution

Solution:

Here is a step-by-step analysis. Main-group elements are those in the s- and p-blocks (Groups 1–2 and 13–18), i.e. their valence shell contains only s and/or p electrons (no partially filled d or f subshells).

1. A. [Ne] $3s^1$
   – Valence configuration $3s^1$ ⇒ s-block, Group 1 ⇒ **main-group**.

2. B. [Ar] $3d^3$ $4s^2$
   – Partially filled 3d ⇒ d-block (transition metal) ⇒ **not** main-group.

3. C. [Kr] $4d^{10}$ $5s^2$ $5p^5$
   – Valence in 5s and 5p ⇒ p-block, Group 17 (halogen) ⇒ **main-group**.

4. D. [Ar] $3d^{10}$ $4s^1$
   – This is Cu, a transition metal in the d-block ⇒ **not** main-group.

5. E. [Rn] $5f^0$ $6d^2$ $7s^2$
   – Th lies in the actinide (f-block) series ⇒ **not** main-group.

Hence only A and C are main-group elements.

Answer: (2) A and C only.

54 Problem 54

Dalton's Atomic theory could not explain which of the following?

(1) Law of conservation of mass

(2) Law of constant proportion

(3) Law of multiple proportion

(4) Law of gaseous volume

Hide Solution

Solution:

Here is a detailed, step-by-step analysis of which law Dalton’s atomic theory could not explain.

Step 1. Recall the main postulates of Dalton’s atomic theory

1. Matter is made of indivisible atoms.
2. All atoms of a given element are identical in mass and properties.
3. Compounds are formed by a combination of atoms of different elements in simple whole-number ratios.
4. In chemical reactions, atoms are neither created nor destroyed—only rearranged.

Step 2. Check each law against Dalton’s ideas

(1) Law of conservation of mass
“Mass is neither created nor destroyed in a chemical reaction.”
– Dalton’s postulate 4 says atoms simply rearrange, so total mass stays constant.
⇒ Dalton’s theory fully explains this law.

(2) Law of constant (definite) proportions
“A given compound always contains the same elements in exactly the same mass ratio.”
– Since a compound is built from a fixed number of each type of atom (postulate 3), the mass ratio is fixed.
⇒ Dalton’s theory explains this law.

(3) Law of multiple proportions
“When two elements form more than one compound, the masses of one element that combine with a fixed mass of the other are simple whole-number multiples of each other.”
– Again, different compounds correspond to different whole-number combinations of atoms.
⇒ Dalton himself used this law as key evidence for his atomic theory, so it is explained.

(4) Law of gaseous volumes (Gay-Lussac’s law of combining volumes)
“At constant temperature and pressure, the volumes of reacting gases and their gaseous products bear simple whole-number ratios.”

$$\frac{V_{\text{gas }1}}{V_{\text{gas }2}} = \text{small whole number } (1{:}1,\ 1{:}2,\ 2{:}1,\ \ldots).$$

Why Dalton’s theory fails here
– Dalton pictured gases as collections of indivisible atoms and never introduced the idea that **equal volumes** of gases contain **equal numbers of particles**.
– Without that hypothesis (later proposed by Avogadro), one cannot relate volumes directly to numbers of atoms or molecules.

⇒ **Dalton’s atomic theory could not explain the law of gaseous volumes.**

Answer: (4) Law of gaseous volume.

55 Problem 55

Consider the following compounds: KO_2, H_2O_2 and H_2SO_4. The oxidation states of the underlined elements in them are, respectively,

(1) +1, -1, and +6

(2) +2, -2, and +6

(3) +1, -2, and +4

(4) +4, -4, and +6

Hide Solution

Solution:

Here is a detailed, step-by-step solution. We shall assume that in KO_2 the underlined element is K, in H_2O_2 it is O, and in H_2SO_4 it is S, so that our goal is to find
– the oxidation state of K in KO_2,
– the oxidation state of O in H_2O_2,
– the oxidation state of S in H_2SO_4.

Step 1. Oxidation state of K in KO_2
KO_2 is neutral, so the sum of oxidation numbers is zero. We recall that KO_2 is the superoxide salt, in which the (O_2) unit carries a total charge of –1. Let x be the oxidation state of K. Then

$$x + (\text{charge on } \mathrm{O}_2) \;=\; 0 \quad\Longrightarrow\quad x + (-1) = 0 \quad\Longrightarrow\quad x = +1.$$

Thus K is in the +1 state.

Step 2. Oxidation state of O in H_2O_2
Hydrogen peroxide H_2O_2 is a neutral molecule. Let y be the oxidation state of each O atom (they are equivalent). Hydrogen in almost all compounds is +1. Hence

$$2\,(+1) \;+\; 2\,y \;=\; 0 \quad\Longrightarrow\quad 2 + 2y = 0 \quad\Longrightarrow\quad y = -1.$$

So each O is –1.

Step 3. Oxidation state of S in H_2SO_4
Sulfuric acid H_2SO_4 is neutral. Let z be the oxidation state of S. We know H is +1 and O is –2. Thus

$$2\,(+1) \;+\; z \;+\; 4\,(-2) \;=\; 0 \quad\Longrightarrow\quad 2 + z - 8 = 0 \quad\Longrightarrow\quad z = +6.$$

Putting these results together, the oxidation states of the underlined elements are

$$\mathrm{K \text{ in } KO_2}:\; +1, \quad \mathrm{O \text{ in } H_2O_2}:\; -1, \quad \mathrm{S \text{ in } H_2SO_4}:\; +6.$$

This corresponds to choice (1).

56 Problem 56

If the half-life ($t_{1/2}$) for a first order reaction is 1 minute, then the time required for 99.9% completion of the reaction is closest to:

(1) 2 minutes

(2) 4 minutes

(3) 5 minutes

(4) 10 minutes

Hide Solution

Solution:

Here is a detailed step-by-step solution.

Step 1: Recall the integrated rate law for a first-order reaction
For a reactant A undergoing first-order decay

$$\frac{d[A]}{dt} = -k\,[A]$$

the integrated form is

$$\ln\frac{[A]}{[A]_0} = -k\,t\,,$$

or equivalently

$$\ln\frac{[A]_0}{[A]} = k\,t\,.$$

Step 2: Relate the half-life to the rate constant
The half-life $t_{1/2}$ for a first-order reaction is given by

$$t_{1/2} = \frac{\ln 2}{k}\,.$$

We are told $t_{1/2} = 1\ \mathrm{min}$, so

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.6931}{1\ \mathrm{min}} = 0.6931\ \mathrm{min}^{-1}\,.$$

Step 3: Determine the fraction remaining after 99.9% completion
“99.9% completion” means 99.9% of A has reacted, so the fraction remaining is

$$\frac{[A]}{[A]_0} = 1 - 0.999 = 0.001\,.$$

Step 4: Solve for the time t
Use

$$\ln\frac{[A]_0}{[A]} = k\,t\,.$$

Substitute $\frac{[A]_0}{[A]} = \frac{1}{0.001} = 1000$ and $k = 0.6931\ \mathrm{min}^{-1}$:

$$t = \frac{1}{k}\ln\bigl(1000\bigr) = \frac{1}{0.6931}\ln\bigl(10^3\bigr) = \frac{1}{0.6931}\,(3\ln 10) = \frac{3\times 2.3026}{0.6931} \approx 9.97\ \mathrm{min}\,.$$

Step 5: Choose the closest answer
The time required is approximately 10 minutes. Hence the best choice is

(4) 10 minutes.

57 Problem 57

The correct order of the wavelength of light absorbed by the following complexes is, A. $[Co(NH_3)_6]^{3+}$ B. $[Co(CN)_6]^{3-}$ C. $[Cu(H_2O)_4]^{2+}$ D. $[Ti(H_2O)_6]^{3+}$ Choose the correct answer from the options given below:

(1) B < D < A < C

(2) B < A < D < C

(3) C < D < A < B

(4) C < A < D < B

Hide Solution

Solution:

Solution.

Step 1. List the complexes and note the ligands and oxidation states
A. $[Co(NH_3)_6]^{3+}$ (ligand: NH_3; metal: Co^{3+})
B. $[Co(CN)_6]^{3-}$ (ligand: CN^-; metal: Co^{3+})
C. $[Cu(H_2O)_4]^{2+}$ (ligand: H_2O; metal: Cu^{2+})
D. $[Ti(H_2O)_6]^{3+}$ (ligand: H_2O; metal: Ti^{3+})

Step 2. Recall the spectrochemical series (increasing field strength)

$$\cdots < H_2O < NH_3 < CN^- < \cdots$$

A stronger-field ligand produces a larger crystal-field splitting Δ.

Step 3. Effect of oxidation state
For a given ligand, a higher metal oxidation state also increases Δ.
Thus for the aqua complexes

$$\Delta\big([Ti(H_2O)_6]^{3+}\big)\ >\ \Delta\big([Cu(H_2O)_4]^{2+}\big).$$

Step 4. Rank the Δ values

1. B: $[Co(CN)_6]^{3-}$ has the strongest ligand (CN^-) on Co^{3+} $\Rightarrow$ largest Δ.
2. A: $[Co(NH_3)_6]^{3+}$ is next (NH_3 on Co^{3+}).
3. D: $[Ti(H_2O)_6]^{3+}$ (water on Ti^{3+})
4. C: $[Cu(H_2O)_4]^{2+}$ (water on Cu^{2+})

Hence

$$\Delta(B) > \Delta(A) > \Delta(D) > \Delta(C).$$

Step 5. Relate splitting Δ to absorption wavelength λ
Since the absorbed photon energy $E \propto \Delta$ and $E = hc/\lambda$, a larger Δ corresponds to a shorter wavelength λ. Therefore

$$\lambda(B) < \lambda(A) < \lambda(D) < \lambda(C).$$

This matches option (2).

Answer: (2) $\quad B < A < D < C.$

58 Problem 58

Which one of the following compounds can exist as cis-trans isomers?

(1) Pent-1-ene

(2) 2-Methylhex-2-ene

(3) 1,1-Dimethylcyclopropane

(4) 1,2-Dimethylcyclohexane

Hide Solution

Solution:

Here's the step-by-step analysis. Recall:

1. An alkene C=C can show cis–trans isomerism only if each sp²-carbon bears two *different* substituents.
2. A cycloalkane can show cis–trans isomerism whenever two substituents are on *different* ring-carbons, since rotation about C–C bonds in the ring is restricted.

Now examine each choice:

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1. Pent-1-ene

Structural formula:

$$\mathrm{CH_2 = CH - CH_2 - CH_2 - CH_3}$$

At the left sp²-carbon (C-1) the two substituents are both H's ($\mathrm{CH_2}$), so they are *identical*. Hence C-1 does *not* have two different groups → **no** cis–trans.

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2. 2-Methylhex-2-ene

Structural formula:

$$\mathrm{CH_3\ -\ C(CH_3) = CH\ -\ CH_2 - CH_2 - CH_3}$$

- Left sp²-carbon (C-2) bears substituents $\mathrm{CH_3}$ (from the main chain) and another $\mathrm{CH_3}$ (the methyl substituent) → *identical* → no stereochemistry.
- Even though the right sp²-carbon has H vs. $\mathrm{CH_2CH_2CH_3}$, the left fails the "two different groups" test → **no** cis–trans.

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3. 1,1-Dimethylcyclopropane

Substituents: two methyls on the *same* carbon (C-1). Geometric (cis vs. trans) requires substituents on *different* carbons in a ring → **no** cis–trans.

---

4. 1,2-Dimethylcyclohexane

Substituents on adjacent carbons C-1 and C-2 in a cyclohexane ring. Rotation about C–C in the ring is restricted, so you can have:
– **cis**-1,2 (both methyls "up" or both "down")
– **trans**-1,2 (one "up," one "down")
Thus **yes**, this pair exists as genuine geometric isomers.

Answer:
The only compound that can exist as cis–trans isomers is

$$\boxed{\text{1, 2-Dimethylcyclohexane}} \quad (\text{option } 4).$$

59 Problem 59

Phosphoric acid ionizes in three steps with their ionization constant values K_a_1, K_a_2 and K_a_3, respectively, while K is the overall ionization constant. Which of the following statements are true? A. log K = log K_a_1 + log K_a_2 + log K_a_3 B. H_3PO_4 is a stronger acid than $H_2PO_4^-$ and HPO_4^{2-}. C. K_a_1 > K_a_2 > K_a_3 D. K_a_1 = (K_a_3 ≠ K_a_2) / 2 Choose the correct answer from the options given below:

(1) A and B only

(2) A and C only

(3) B, C and D only

(4) A, B and C only

Hide Solution

Solution:

Here is the detailed solution:

Step 1. Write the three stepwise ionizations of H_3PO_4 and their constants

1) $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$, constant = Ka_1
2) $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$, constant = Ka_2
3) $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$, constant = Ka_3

Step 2. Express the overall ionization constant

Overall reaction:

$$\mathrm{H_3PO_4} \rightleftharpoons 3\mathrm{H}^+ + \mathrm{PO}_4^{3-}$$

The overall equilibrium constant is the product of the stepwise constants:

$$K = K_{a1} \times K_{a2} \times K_{a3}$$

Step 3. Take logarithms

$$\log K = \log\left(K_{a1}K_{a2}K_{a3}\right) = \log K_{a1} + \log K_{a2} + \log K_{a3}$$

This shows statement A is true.

Step 4. Compare acid strengths

By definition, the larger the K_a the stronger the acid. Since successive proton removals become harder, one finds

$$K_{a1} > K_{a2} > K_{a3}$$

Thus H_3PO_4 (with K_{a1}) is the strongest acid, then $H_2PO_4^-$, then HPO_4^{2-}. This makes statements B and C true.

Step 5. Check statement D

D asserts some numerical relation among K_{a1}, K_{a2}, K_{a3} that does not follow from any known property of phosphoric acid. It is false.

Conclusion: A, B and C are true, D is false. Hence the correct choice is

(4) A, B and C only.

61 Problem 61

If the molar conductivity (Λ_m) of a 0.050 mol L^{-1} solution of a monobasic weak acid is 90 S cm^2 mol^{-1}, its extent (degree) of dissociation will be [Assume λ_+° = 349.6 S cm^2 mol^{-1} and λ_-° = 50.4 S cm^2 mol^{-1}.]

(1) 0.115

(2) 0.125

(3) 0.225

(4) 0.215

Hide Solution

Solution:

Here is a step-by-step solution:

1. Write the dissociation of a monobasic weak acid HA:

$$\mathrm{HA} \rightleftharpoons \mathrm{H}^+ + \mathrm{A}^-.$$

2. Define the degree of dissociation α. If the analytical concentration is c, then at equilibrium

$$[\mathrm{H}^+] = c\,\alpha, \quad [\mathrm{A}^-] = c\,\alpha, \quad [\mathrm{HA}] = c\,(1-\alpha)\,.$$

3. The molar conductivity Λ_m at concentration c (assuming the ionic mobilities are at their infinite-dilution values) is given by the sum of the contributions of the ions actually present in solution. Undissociated HA does not conduct, so

$$\Lambda_m = \underbrace{c\,\alpha}_{[\mathrm{H}^+]}\frac{\lambda_+^\circ}{c} + \underbrace{c\,\alpha}_{[\mathrm{A}^-]}\frac{\lambda_-^\circ}{c} = \alpha\,(\lambda_+^\circ + \lambda_-^\circ)\,.$$

Here λ_+° and λ_-° are the limiting molar ionic conductivities of H^+ and A^-, respectively.

4. Solve for the degree of dissociation α:

$$\alpha = \frac{\Lambda_m}{\lambda_+^\circ + \lambda_-^\circ}.$$

5. Substitute the given values:

$$\Lambda_m = 90 \text{ S cm}^2 \text{ mol}^{-1}, \quad \lambda_+^\circ = 349.6 \text{ S cm}^2 \text{ mol}^{-1}, \quad \lambda_-^\circ = 50.4 \text{ S cm}^2 \text{ mol}^{-1}.$$

Hence

$$\alpha = \frac{90}{349.6 + 50.4} = \frac{90}{400} = 0.225.$$

Answer: 0.225 (option 3).

62 Problem 62

Given below are two statements: Statement I: A hypothetical diatomic molecule with bond order zero is quite stable. Statement II: As bond order increases, the bond length increases. In the light of the above statements, choose the most appropriate answer from the options given below:

(1) Both Statement I and Statement II are true

(2) Both Statement I and Statement II are false

(3) Statement I is true but Statement II is false

(4) Statement I is false but Statement II is true

Hide Solution

Solution:

Here’s a step-by-step analysis of the two statements:

1. Recall the definition of bond order in Molecular Orbital (MO) theory:

$$\text{Bond order} = \frac{N_b - N_a}{2}$$

where N_b is the number of electrons in bonding orbitals and N_a is the number in antibonding orbitals.

2. Stability vs. bond order zero
– If a diatomic molecule has bond order zero, that means

$$N_b - N_a = 0 \quad \Longrightarrow \quad N_b = N_a.$$

– In that case there is no net bonding interaction, so the “molecule” will not hold together; it is not stable.
⇒ Statement I (“A hypothetical diatomic molecule with bond order zero is quite stable.”) is **false**.

3. Bond length vs. bond order
– Empirically and from MO theory, *as bond order increases*, more electrons occupy bonding orbitals relative to antibonding ones, pulling the nuclei closer together.
– Thus higher bond order ⇒ stronger, *shorter* bonds.
⇒ The claim “As bond order increases, the bond length increases” is the opposite of what actually happens. Statement II is **false**.

4. Conclusion
Both Statement I and Statement II are false.

Answer choice: **(2) Both Statement I and Statement II are false**.

63 Problem 63

Out of the following complex compounds, which of the compound will be having the minimum conductance in solution?

(1) $[\mathrm{Co(NH_3)_3Cl_3}]$

(2) $[\mathrm{Co(NH_3)_4Cl_2}]$

(3) $[\mathrm{Co(NH_3)_6]Cl_3}$

(4) $[\mathrm{Co(NH_3)_5Cl]Cl}$

Hide Solution

Solution:

Here is a step-by-step analysis. Remember that the conductance of an aqueous solution is essentially proportional to the total number of ions produced on dissolution. Any ligand that sits inside the coordination sphere does **not** give rise to free ions; only counter-ions (those written outside the brackets) appear as mobile ions in solution.

1. Write down how each complex ionizes in water and count the ions.

(1) $[\mathrm{Co}(NH_3)_3Cl_3]$
All three chlorides are coordinated, so there are no counter-ions.

$$[\mathrm{Co}(NH_3)_3Cl_3] \longrightarrow \text{no dissociation} \quad \Rightarrow \text{0 ions}$$

(2) $[\mathrm{Co}(NH_3)_4Cl_2]$
Both chlorides are inside the coordination sphere; again no counter-ions.

$$[\mathrm{Co}(NH_3)_4Cl_2] \longrightarrow \text{no dissociation} \quad \Rightarrow \text{0 ions}$$

(3) $[\mathrm{Co}(NH_3)_6]Cl_3$
Here the complex cation is $[\mathrm{Co}(NH_3)_6]^{3+}$ and there are three Cl$^-$ counter-ions.

$$[\mathrm{Co}(NH_3)_6]Cl_3 \longrightarrow [\mathrm{Co}(NH_3)_6]^{3+} + 3\,Cl^- \quad \Rightarrow 1+3=4 \text{ ions}$$

(4) $[\mathrm{Co}(NH_3)_5Cl]Cl$
The cation is $[\mathrm{Co}(NH_3)_5Cl]^{2+}$ with one Cl$^-$ as counter-ion.

$$[\mathrm{Co}(NH_3)_5Cl]Cl \longrightarrow [\mathrm{Co}(NH_3)_5Cl]^{2+} + Cl^- \quad \Rightarrow 1+1=2 \text{ ions}$$

2. Compare the total ions produced:
   (1) → 0 ions
   (2) → 0 ions
   (3) → 4 ions
   (4) → 2 ions

3. Since conductance ∝ number of ions, the **minimum** conductance comes from the complexes that give **zero** ions in solution, namely (1) and (2).

Answer: Compounds (1) $[\mathrm{Co}(NH_3)_3Cl_3]$ and (2) $[\mathrm{Co}(NH_3)_4Cl_2]$ have the minimum conductance (they are non-electrolytes).

64 Problem 64

Match List - I with List - II List-I | List-II :-- | :-- A. $\mathrm{XeO_3}$ | I. $\mathrm{sp^3\ d}$; linear B. $\mathrm{XeF_2}$ | II. $\mathrm{sp^3}$; pyramidal C. $\mathrm{XeOF_4}$ | III. $\mathrm{sp^3\ d^3}$; distorted octahedral D. $\mathrm{XeF_6}$ | IV. $\mathrm{sp^3\ d^2}$; square pyramidal

(1) A-II, B-I, C-IV, D-III

(2) A-II, B-I, C-III, D-IV

(3) A-IV, B-II, C-III, D-I

(4) A-IV, B-II, C-I, D-III

Hide Solution

Solution:

Here is the detailed solution. We will for each compound (i) count its total valence-electron pairs, (ii) determine the number of electron-pair domains around Xe, (iii) assign the corresponding hybridization, and (iv) state the molecular shape.

1. XeO_3
  – Total valence electrons: Xe (8) + 3·O (3·6) = 8 + 18 = 26 e^- ⇒ 13 pairs.
  – We draw three Xe=O double bonds (each uses 2 pairs ⇒ 3·2 = 6 pairs) leaving 7 pairs.
  – Each O needs 2 lone pairs (3·2 = 6 pairs), leaving 1 pair on Xe.
  – Electron-pair domains on Xe = 3 (Xe–O bonds) + 1 (lone pair) = 4 ⇒ sp^3.
  – Molecular shape with one lone pair and three bonds = trigonal pyramidal.

  ⇒ XeO_3: sp^3, pyramidal ⇒ matches List-II II.

2. XeF_2
  – Valence electrons: Xe (8) + 2·F (2·7) = 8 + 14 = 22 e^- ⇒ 11 pairs.
  – Two Xe–F bonds use 2 pairs, leaving 9 pairs.

– Each F takes 3 lone pairs (2·3 = 6 pairs), leaving 3 pairs on Xe.
– Domains on Xe = 2 bonds + 3 lone pairs = 5 ⇒ sp^3d.
– With three lone pairs occupying equatorial sites in a trigonal bipyramid, the shape is linear.

⇒ XeF_2: sp^3d, linear ⇒ matches List-II I.

3. $XeOF_4$
– Valence electrons: Xe (8) + O (6) + 4·F (4·7) = 8 + 6 + 28 = 42 e^- ⇒ 21 pairs.
– We draw 4 Xe–F bonds (4 pairs) and one Xe=O double bond (2 pairs), using 6 pairs, leaving 15.
– Four F atoms take 3 lone pairs each (4·3 = 12 pairs), O takes 2 lone pairs (2 pairs), leaving 1 pair on Xe.
– Domains on Xe = 5 bonds + 1 lone pair = 6 ⇒ sp^3d^2.
– With one lone pair in an octahedral array, the molecular shape is square pyramidal.

⇒ $XeOF_4$: sp^3d^2, square pyramidal ⇒ matches List-II IV.

4. XeF_6
– Valence electrons: Xe (8) + 6·F (6·7) = 8 + 42 = 50 e^- ⇒ 25 pairs.
– Six Xe–F bonds use 6 pairs, leaving 19 pairs.
– Six F atoms take 3 lone pairs each (6·3 = 18 pairs), leaving 1 pair on Xe.
– Domains on Xe = 6 bonds + 1 lone pair = 7 ⇒ sp^3d^3.
– Seven-domain electron geometry is pentagonal bipyramidal, but with one lone pair the observed molecular shape is a distorted octahedron.

⇒ XeF_6: sp^3d^3, distorted octahedral ⇒ matches List-II III.

Putting it all together:

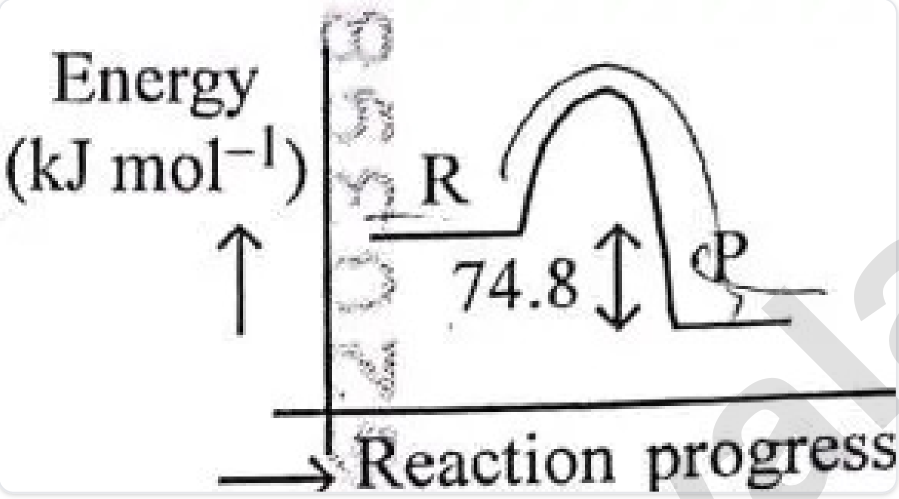
A. XeO_3 → II
B. XeF_2 → I
C. $XeOF_4$ → IV
D. XeF_6 → III

This is choice (1).

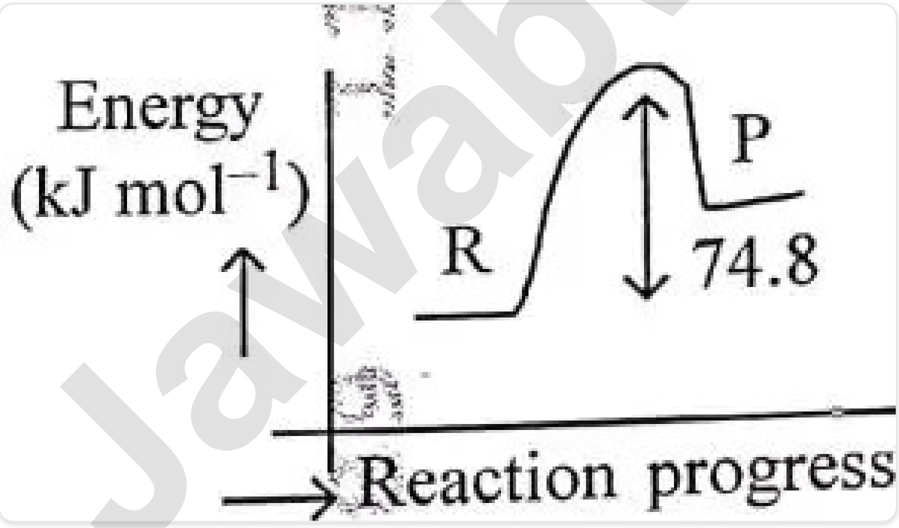
65 Problem 65

$C(s) + 2H_2(g) \rightarrow CH_4(g); \Delta H = -74.8\ kJ\ mol^{-1}$ Which of the following diagrams gives an accurate representation of the above reaction? [$R \rightarrow$ reactants; $P \rightarrow$ products]

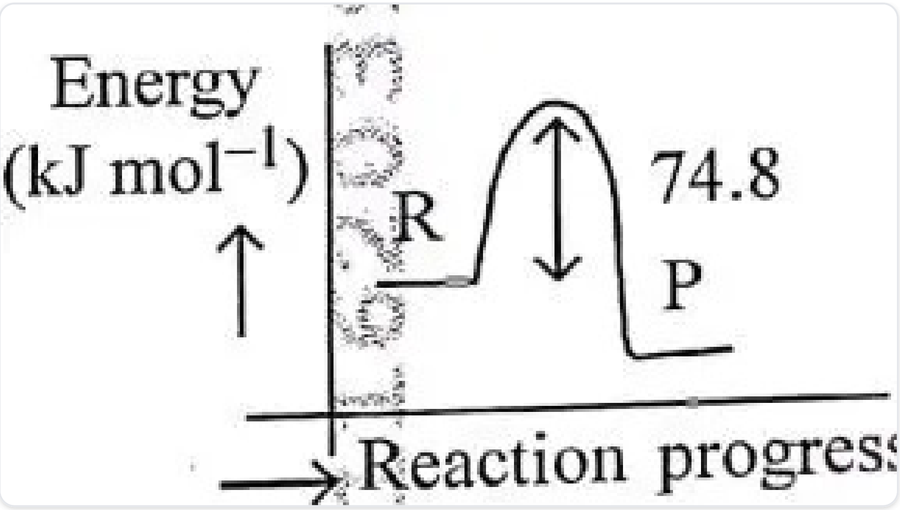
(1)



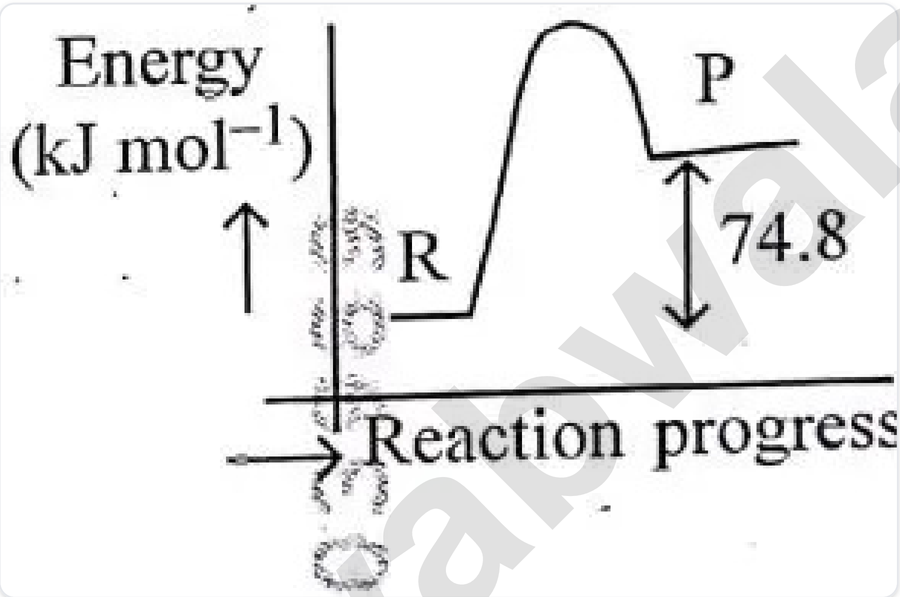
(2)



(3)



(4)



Hide Solution

Solution:

Here is a detailed, step-by-step analysis:

1. Write down the given reaction and its enthalpy change:

$$C_{(s)} + 2\,H_{2(g)} \longrightarrow CH_{4(g)} \quad \Delta H = -74.8 \text{ kJ mol}^{-1}.$$

2. Interpret the sign of ΔH:
   $\Delta H < 0$ means the reaction is exothermic. In an energy-profile (reaction-

coordinate) diagram that means

$$H_{\text{products}} \; < \; H_{\text{reactants}},$$

and the vertical drop between reactants and products should be 74.8 kJ mol^{-1}.

3. Sketching the general shape of an exothermic profile:
   – On the left (reactants) you start at some energy level.
   – You climb up to the transition-state (the “hump”) – this difference is the activation energy.
   – You then fall to a lower energy level (products).
   – The vertical difference between reactants and products is $|\Delta H| = 74.8$ kJ mol^{-1}.

4. Compare with the four choices. The only diagram that shows
   a) a single hump (activation barrier),
   b) products lower than reactants by 74.8 kJ,
   c) an arrow correctly indicating a 74.8 kJ drop from reactants to products
   is choice (4).

Therefore the correct energy-profile diagram is option (4).

66 Problem 66

Match List - I with List - II List-I (Example) | List-II (Type of Solution) :-- | :-- A. Humidity | I. Solid in solid B. Alloys | II. Liquid in gas C. Amalgams | III. Solid in gas D. Smoke | IV. Liquid in solid

(1) A-II, B-IV, C-I, D-III

(2) A-II, B-I, C-IV, D-III

(3) A-III, B-I, C-IV, D-II

(4) A-III, B-II, C-I, D-IV

Hide Solution

Solution:

Here is a step-by-step classification of each example into the “solute + solvent” type and the matching of List-I to List-II:

Step 1: Recall the possible types of solutions by physical state
I. Solid in solid
II. Liquid in gas
III. Solid in gas
IV. Liquid in solid

Step 2: Classify each example

1. Humidity
   – Humidity is moisture (tiny droplets of water, i.e. liquid) dispersed in air (gas).
   – Type ⇒ Liquid in gas ⇒ II

2. Alloys
   – An alloy is a homogeneous mixture of one or more metals (all solids) with other metals or non-metals (also solids).
   – Type ⇒ Solid in solid ⇒ I

3. Amalgams
   – An amalgam is an alloy in which mercury (a liquid metal) dissolves in a solid metal.
   – Type ⇒ Liquid in solid ⇒ IV

4. Smoke
   – Smoke consists of fine solid particles dispersed in a gas.
   – Type ⇒ Solid in gas ⇒ III

Step 3: Write down the matching A–D → I–IV

$$
\begin{gathered}
A.\ \text{Humidity} \to \text{II (Liquid in gas)} \\
B.\ \text{Alloys} \to \text{I (Solid in solid)} \\
C.\ \text{Amalgams} \to \text{IV (Liquid in solid)} \\
D.\ \text{Smoke} \to \text{III (Solid in gas)}
\end{gathered}
$$

Step 4: Choose the correct option
Comparing with the given options, we get

$$\boxed{(2)\ A-II,\ B-I,\ C-IV,\ D-III.}$$

67 Problem 67

The correct order of decreasing basic strength of the given amines is :

(1) N -methylaniline > benzenamine > ethanamine > N-ethylethanamine

(2) N -ethylethanamine > ethanamine > benzenamine > N -methylaniline

(3) N -ethylethanamine > ethanamine > N -methylaniline > benzenamine

(4) benzenamine > ethanamine > N -methylaniline > N-ethylethanamine

Hide Solution

Solution:

Here is a detailed, step-by-step comparison of the basicities of the four amines.

Step 1. Recall that in water the strength of a base B is related to the acidity of its conjugate acid BH$^+$. Specifically, the larger the pK_a of BH$^+$, the stronger the base B.

Base strength order ⇔ higher $pK_a(\mathrm{BH}^+)$ ⇒ stronger B.

Step 2. Write the protonation equilibrium common to all amines:

$$\mathrm{RNH_2} + H^+ \longrightarrow \mathrm{RNH_3^+}$$

Step 3. List the four amines and their approximate pK_a values for the conjugate acids (at 25 °C):

1. Benzenamine (aniline), $\mathrm{PhNH_2}$

$$pK_a(\mathrm{PhNH_3^+}) \approx 4.6$$

(very weak base because the lone pair on N is delocalized into the aromatic ring)

2. N-Methylaniline, PhNHMe

$$pK_a(\mathrm{PhNHMe^+}) \approx 5.1$$

(slightly more basic than aniline due to the +I effect of Me, but still resonance-deactivated)

3. Ethanamine (ethylamine), $\mathrm{EtNH_2}$

$$pK_a(\mathrm{EtNH_3^+}) \approx 10.7$$

(stronger base because alkyl groups donate electron density by inductive and hyperconjugation effects)

4. N-Ethylethanamine (diethylamine), $\mathrm{Et_2NH}$

$$pK_a(\mathrm{Et_2NH_2^+}) \approx 11.0$$

(even stronger base, two alkyl groups donate more electron density)

Step 4. Rank them in order of decreasing base strength (i.e.\ highest pK_a first):

$$\underbrace{\mathrm{Et_2NH}}_{pK_a \approx 11.0} > \underbrace{\mathrm{EtNH_2}}_{pK_a \approx 10.7} > \underbrace{\mathrm{PhNHMe}}_{pK_a \approx 5.1} > \underbrace{\mathrm{PhNH_2}}_{pK_a \approx 4.6}$$

Step 5. Match this order to the given choices. Choice (3) reads:
"N-ethylethanamine > ethanamine > N-methylaniline > benzenamine."

Hence the correct answer is choice (3).

68 Problem 68

Among the following, choose the ones with equal number of atoms. A. 212 g of $\mathrm{Na_2CO_3}$ (s) [molar mass $= 106\ \mathrm{g}$] B. 248 g of $\mathrm{Na_2O}$ (s) [molar mass $= 62\ \mathrm{g}$] C. 240 g of NaOH (s) [molar mass $= 40\ \mathrm{g}$] D. 12 g of $\mathrm{H_2(\ g)}$ [molar mass $= 2\ \mathrm{g}$] E. 220 g of $\mathrm{CO_2(\ g)}$ [molar mass $= 44\ \mathrm{g}$]

(1) A, B, and C only

(2) A, B, and D only

(3) B, C, and D only

(4) B, D, and E only

Hide Solution

Solution:

Here is a step-by-step solution.

Step 1: Compute the number of moles of each substance.
For a sample of mass m and molar mass M,

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

A. Na_2CO_3:

$$n_A = \frac{212\,\mathrm{g}}{106\,\mathrm{g/mol}} = 2.00\,\mathrm{mol}.$$

B. Na_2O:

$$n_B = \frac{248\,\mathrm{g}}{62\,\mathrm{g/mol}} = 4.00\,\mathrm{mol}.$$

C. NaOH:

$$n_C = \frac{240\,\mathrm{g}}{40\,\mathrm{g/mol}} = 6.00\,\mathrm{mol}.$$

D. H_2:

$$n_D = \frac{12\,\mathrm{g}}{2\,\mathrm{g/mol}} = 6.00\,\mathrm{mol}.$$

E. CO_2:

$$n_E = \frac{220\,\mathrm{g}}{44\,\mathrm{g/mol}} = 5.00\,\mathrm{mol}.$$

Step 2: Count the number of atoms per formula unit.
A. Na_2CO_3: $2\ (\mathrm{Na}) + 1\ (\mathrm{C}) + 3\ (\mathrm{O}) = 6$ atoms.
B. Na_2O: $2 + 1 = 3$ atoms.
C. NaOH: $1 + 1 + 1 = 3$ atoms.
D. H_2: 2 atoms.
E. CO_2: $1 + 2 = 3$ atoms.

Step 3: Compute total moles of atoms in each sample.

$$\text{moles of atoms} = n \times (\text{atoms per formula unit}).$$

A. $2.00\,\text{mol} \times 6 = 12.0\,\text{mol}\,(\text{atoms})$.
B. $4.00\,\text{mol} \times 3 = 12.0\,\text{mol}\,(\text{atoms})$.
C. $6.00\,\text{mol} \times 3 = 18.0\,\text{mol}\,(\text{atoms})$.
D. $6.00\,\text{mol} \times 2 = 12.0\,\text{mol}\,(\text{atoms})$.
E. $5.00\,\text{mol} \times 3 = 15.0\,\text{mol}\,(\text{atoms})$.

Step 4: Compare the total numbers of atoms.
A, B, and D each have 12.0 mol of atoms, while C has 18.0 mol and E has 15.0 mol.

Therefore the samples with equal number of atoms are A, B, and D.
Answer: (2) A, B, and D only.

69 Problem 69

Match List I with List II. | List I (Name of Vitamin) | List II (Deficiency disease) | | :----------------------- | :------------------------- | | A. Vitamin B_{12} | I. Cheilosis | | B. Vitamin D | II. Convulsions | | C. Vitamin B_2 | III. Rickets | | D. Vitamin B_6 | IV. Pernicious anaemia |

(1) A-I, B-III, C-II, D-IV

(2) A-IV, B-III, C-I, D-II

(3) A-II, B-III, C-I, D-IV

(4) A-IV, B-III, C-II, D-I

Hide Solution

Solution:

Here's the detailed matching with explanations:

Step 1: Recall the deficiency symptoms of each vitamin
1. Vitamin B_{12}
   - Required for DNA synthesis and red-cell maturation.
   - Deficiency ⇒ megaloblastic, particularly pernicious, anaemia.

   ⇒ matches IV (Pernicious anaemia).

2. Vitamin D
   - Regulates Ca^{2+} and PO_4^{3-} homeostasis and bone mineralization.
   - Deficiency in children ⇒ rickets.

   ⇒ matches III (Rickets).

3. Vitamin B_2 (riboflavin)
   - Component of FAD and FMN; important in redox reactions.
   - Deficiency ⇒ cheilosis (angular stomatitis), glossitis, seborrhoeic dermatitis.

   ⇒ matches I (Cheilosis).

4. Vitamin B_6 (pyridoxine)
   - Cofactor in amino-acid metabolism, neurotransmitter synthesis.
   - Severe deficiency ⇒ seizures/convulsions.

   ⇒ matches II (Convulsions).

Step 2: Collect the matches
A. $B_{12} \to$ IV
B. D $\to$ III
C. $B_2 \to$ I
D. $B_6 \to$ II

Step 3: Choose the correct option

$$\boxed{(2)\ \ A\text{-}IV,\ B\text{-}III,\ C\text{-}I,\ D\text{-}II}$$

70 Problem 70

The correct order of decreasing acidity of the following aliphatic acids is :

(1) $\mathrm{(CH_3)_3CCOOH > (CH_3)_2CHCOOH > CH_3COOH > HCOOH}$

(2) $\mathrm{CH_3COOH > (CH_3)_2CHCOOH > (CH_3)_3CCOOH > HCOOH}$

(3) $\mathrm{HCOOH > CH_3COOH > (CH_3)_2CHCOOH > (CH_3)_3CCOOH}$

(4) $\mathrm{HCOOH > (CH_3)_3CCOOH > (CH_3)_2CHCOOH > CH_3COOH}$

Hide Solution

Solution:

Here is a detailed, step-by-step solution:

Step 1. Recall that the strength of a carboxylic acid
is inversely related to the pK_a of its conjugate base:
the lower the pK_a, the stronger the acid.

Step 2. List the experimental pK_a values for the acids in question:

$$\begin{aligned} \mathrm{HCOOH} &\quad pK_a \approx 3.75, \\ \mathrm{CH_3COOH} &\quad pK_a \approx 4.76, \\ \mathrm{(CH_3)_2CHCOOH} &\quad pK_a \approx 4.86, \\ \mathrm{(CH_3)_3CCOOH} &\quad pK_a \approx 5.03. \end{aligned}$$

Step 3. Understand the inductive effect:
Alkyl groups are electron-releasing ($+I$ effect).
When you attach more alkyl groups to the $-COO^-$ moiety,
they push electron density toward the negatively charged oxygen,

destabilizing the conjugate base and thus making the acid weaker.

Step 4. Order the acids by increasing number of alkyl substituents (i.e.\ by decreasing acid strength):

$$\mathrm{HCOOH} > \mathrm{CH_3COOH} > \mathrm{(CH_3)_2CHCOOH} > \mathrm{(CH_3)_3CCOOH}.$$

Step 5. This corresponds to option (3).

Answer: $\boxed{3}$.

71 Problem 71

Given below are two statements : Statement I : Ferromagnetism is considered as an extreme form of paramagnetism. Statement II : The number of unpaired electrons in a Cr^{2+} ion $(\mathrm{Z}=24)$ is the same as that of a Nd^{3+} ion $(\mathrm{Z}=60)$. In the light of the above statements, choose the correct answer from the options given below :

(1) Both Statement I and Statement II are true

(2) Both Statement I and Statement II are false

(3) Statement I is true but Statement II is false

(4) Statement I is false but Statement II is true

Hide Solution

Solution:

Here is a detailed, step-by-step solution.

1. Statement I: “Ferromagnetism is considered as an extreme form of paramagnetism.”
   - Paramagnetism arises from isolated atoms or ions having unpaired electrons; in an applied field these moments tend to align, giving a small, positive susceptibility χ.
   - Ferromagnetism also involves unpaired-electron moments, but here an additional **exchange interaction** between neighboring spins causes **spontaneous**, long-range alignment even in the absence of a field. The result is a very large (in fact divergent as $T \to 0$) positive susceptibility.
   - In many textbooks one indeed regards ferromagnetism as the “extreme” (strongly cooperative) limiting case of paramagnetism.
   ⇒ Statement I is **true**.

2. Statement II: “The number of unpaired electrons in a Cr^{2+} ion $(Z = 24)$ is the same as that of a Nd^{3+} ion $(Z = 60)$.”

   (a) Cr^{2+}, $Z = 24$:

$$\text{Neutral Cr: } [\mathrm{Ar}]\, 3d^5\, 4s^1.$$

   Remove two electrons (first from 4s, then 3d):

$$\mathrm{Cr}^{2+}:\ [\mathrm{Ar}]\, 3d^4.$$

   A $3d^4$ configuration in the high-spin case has one electron in each of four d–orbitals, so

$$\#\text{unpaired electrons in } \mathrm{Cr}^{2+} = 4.$$

   (b) Nd^{3+}, $Z = 60$:

$$\text{Neutral Nd: } [\mathrm{Xe}]\, 4f^4\, 6s^2.$$

Remove two $6s$ electrons and one $4f$ electron:

$$\mathrm{Nd}^{3+}:\ [\mathrm{Xe}]\,4f^3.$$

A $4f^3$ configuration has three singly-occupied f–orbitals, so

$$\#\text{unpaired electrons in Nd}^{3+}=3.$$

Since $4 \neq 3$, Statement II is **false**.

3. Conclusion: Statement I is true and Statement II is false. Answer choice (3).

72 Problem 72

Match List I with List II List I (Mixture) A. $\mathrm{CHCl_3 + C_6H_5NH_2}$ B. Crude oil in petroleum industry C. Glycerol from spent-lye D. Aniline - water List II (Method of Separation) I. Distillation under reduced pressure II. Steam distillation III. Fractional distillation IV. Simple distillation

(1) A-IV, B-III, C-I, D-II

(2) A-IV, B-III, C-II, D-I

(3) A-III, B-IV, C-I, D-II

(4) A-III, B-IV, C-II, D-I

Hide Solution

Solution:

Here is the step-by-step reasoning:

1. A: $CHCl_3$ (b.p. ≃ 61 °C) + $C_6H_5NH_2$ (b.p. ≃ 184 °C)
   – The two components are miscible but their boiling points differ by well over 50 °C.
   – Such a large Δb.p. means simple distillation suffices.
   ⇒ Method IV (Simple distillation)

2. B: Crude oil (a complex mixture of many hydrocarbons with closely spaced boiling points)
   – To separate into fractions (gasoline, kerosene, diesel, etc.) one uses a long column with many theoretical plates.
   ⇒ Method III (Fractional distillation)

3. C: Glycerol from spent-lye
   – Glycerol b.p. ≃ 290 °C and will decompose if heated that high at 1 atm.
   – By lowering the pressure (vacuum) you can distil it at a much lower temperature without decomposition.
   ⇒ Method I (Distillation under reduced pressure)

4. D: Aniline–water mixture
   – Aniline is only sparingly soluble in water, so the two form two liquid phases.
   – Aniline can be co-distilled with steam at temperatures well below its normal b.p. (steam distillation).
   ⇒ Method II (Steam distillation)

Putting it all together:
A–IV, B–III, C–I, D–II

This corresponds to option **(1)**.

Problem Solutions

View detailed solutions to each problem. Click on "Show Solution" to see the full explanation.

Solutions

Showing 13 of 38 solutions

73 Problem 73

For the reaction $A(g) \rightleftharpoons 2B(g)$, the backward reaction rate constant is higher than the forward reaction rate constant by a factor of 2500, at 1000 K. [Given : $\mathrm{R} = 0.0831\ \mathrm{L\ atm\ mol^{-1}\ K^{-1}}$] $\mathrm{K_p}$ for the reaction at 1000 K is

(1) 83.1

(2) 2.077×10^5

(3) 0.033

(4) 0.021

Hide Solution

Solution:

Here is a detailed step-by-step solution using the given data.

1. Write the reaction and identify forward and reverse rates.
   A(g) ⇌ 2 B(g)
   - Forward rate:

$$v_{\mathrm{f}} = k_{\mathrm{f}}[A]$$

   - Reverse rate:

$$v_{\mathrm{r}} = k_{\mathrm{b}}[B]^2$$

2. At equilibrium,

$$v_{\mathrm{f}} = v_{\mathrm{r}} \quad \Longrightarrow \quad k_{\mathrm{f}}[A]_{\mathrm{eq}} = k_{\mathrm{b}}[B]_{\mathrm{eq}}^2 .$$

   Hence the equilibrium constant in concentration form is

$$K_c = \frac{[B]_{\mathrm{eq}}^2}{[A]_{\mathrm{eq}}} = \frac{k_{\mathrm{f}}}{k_{\mathrm{b}}} .$$

3. Use the given ratio of rate constants.

$$k_{\mathrm{b}} = 2500\, k_{\mathrm{f}} \quad \Longrightarrow \quad \frac{k_{\mathrm{f}}}{k_{\mathrm{b}}} = \frac{1}{2500} = 4.0 \times 10^{-4} .$$

   Thus

$$K_c = 4.0 \times 10^{-4} \quad \left(\mathrm{mol\,L^{-1}}\right)^{\Delta \mathrm{n}}, \quad \Delta \mathrm{n} = 2 - 1 = 1 .$$

4. Convert K_c to K_p using

$$K_p = K_c\,(RT)^{\Delta n} ,$$

where

$$R = 0.0831\ \mathrm{L\,atm\,mol^{-1}K^{-1}}, \quad \mathrm{T} = 1000\ \mathrm{K}, \quad \Delta \mathrm{n} = 1\,.$$

5. Substitute numbers:

$$RT = (0.0831\ \mathrm{L\,atm\,mol^{-1}K^{-1}})(1000\ \mathrm{K}) = 83.1\ \mathrm{L\,atm\,mol^{-1}},$$

$$K_p = (4.0 \times 10^{-4}) \times (83.1) = 0.03324 \approx 0.033.$$

Therefore the equilibrium constant in pressure form at 1000 K is

$$\boxed{K_p \approx 0.033},$$

which corresponds to option (3).

74 Problem 74

Given below are two statements : Statement I : Benzenediazonium salt is prepared by the reaction of aniline with nitrous acid at $273-278\ \mathrm{K}$. It decomposes easily in the dry state. Statement II : Insertion of iodine into the benzene ring is difficult and hence iodobenzene is prepared through the reaction of benzenediazonium salt with KI. In the light of the above statements, choose the most appropriate answer from the options given below :

(1) Both Statement I and Statement II are correct

(2) Both Statement I and Statement II are incorrect

(3) Statement I is correct but Statement II is incorrect

(4) Statement I is incorrect but Statement II is correct

Hide Solution

Solution:

Here is a detailed, step-by-step solution:

1. Diazotization of aniline (Statement I)
   – Aniline ($PhNH_2$) is treated with nitrous acid, which is generated in situ by adding sodium nitrite to cold dil. HCl:

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl\,.$$

   – At $273–278$ K the nitrous acid protonates and loses water to give the nitrosonium ion, NO^+, which then reacts with aniline to give the diazonium salt:

$$PhNH_2 + HNO_2 + HCl \longrightarrow Ph–N \equiv N^+\,Cl^- + 2\,H_2O\,.$$

   – The reaction must be kept at low temperature ($273–278$ K) because benzenediazonium salts decompose on warming or when dry, losing N_2 and giving phenol, aryl cations, etc.
   – Conclusion: Statement I is correct.

2. Difficulty of direct iodination & Sandmeyer route (Statement II)
   – Iodination of benzene by the usual electrophilic route is difficult because I_2 is a poor electrophile and the reaction is reversible: you need an oxidant to generate I^+, and even then yields are low.
   – Instead, iodobenzene is most conveniently prepared from benzenediazonium chloride by treating it with potassium iodide (KI). The diazonium group is an excellent

leaving group, and the reaction proceeds with liberation of nitrogen gas:

$$\mathrm{Ph{-}N_2^+\,Cl^-} + \mathrm{KI} \longrightarrow \mathrm{Ph{-}I} + \mathrm{KCl} + \mathrm{N_2}\uparrow.$$

– This is essentially a Sandmeyer-type substitution, and it cleanly gives iodobenzene.
– Conclusion: Statement II is also correct.

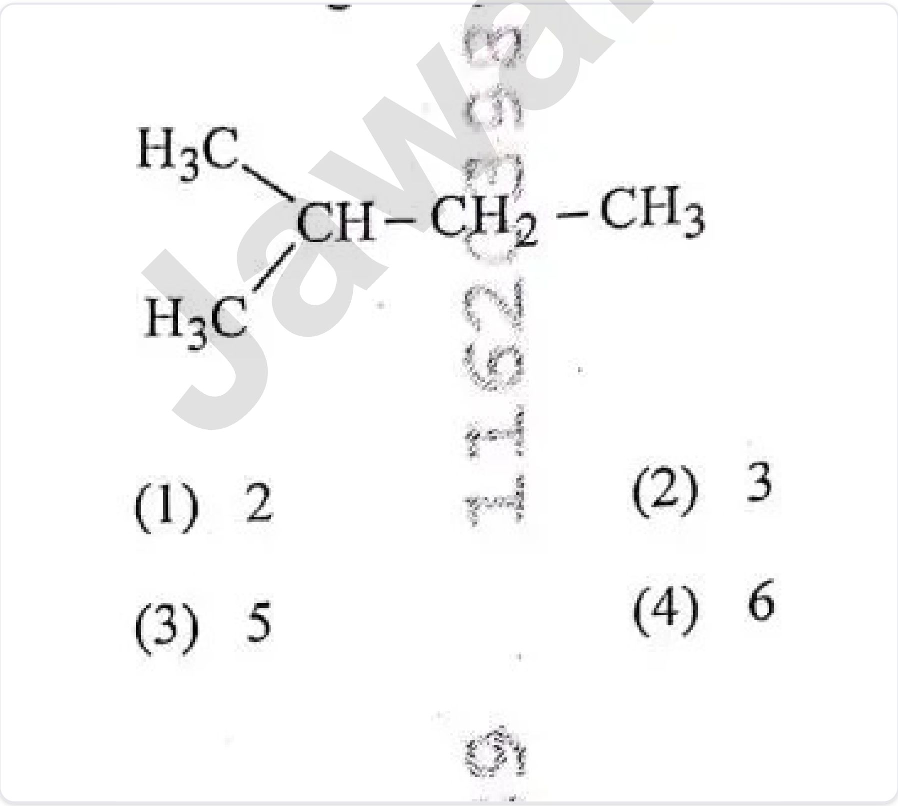
3. Final choice

Since both statements are correct, the correct answer is

$$\boxed{\text{(1) Both Statement I and Statement II are correct.}}$$

75 Problem 75

How many products (including stereoisomers) are expected from monochlorination of the following compound?



(1) 2
(2) 3
(3) 5
(4) 6

(1) 2

(2) 3

(3) 5

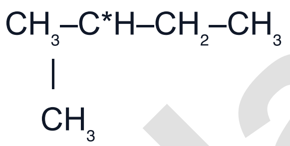
(4) 6

Hide Solution

Solution:

Here’s a step-by-step solution. We recognize the substrate as 2-methylbutane, CH_3–CH(CH_3)–CH_2–CH_3, and we want to count all the distinct mono-chlorination products (including stereoisomers).

1. Number the carbons and identify each kind of hydrogen.
   Let us write the skeleton and label:



$$\begin{array}{l} CH_3\text{–}C^{*}H\text{–}CH_2\text{–}CH_3 \\ \quad\ | \\ \quad CH_3 \end{array}$$

Call the carbon at the star C_2. Then:

- C_1 = the CH_3 (left end)
- C_2 = the CH (tert-C) bearing two CH_3’s (one is the “main-chain” CH_3 at C_1, one is the “branch” CH_3) and one H
- C_3 = the CH_2 (middle of chain)
- C_4 = the terminal CH_3 (right end)

Thus there are three CH_3 groups (on C_1, on the branch off C_2, and at C_4), one CH_2 (at C_3), and one CH (at C_2).

2. Use the internal symmetry to see which H’s are equivalent.

A reflection-plane through the C_2–C_3 axis that bisects the angle between the two methyl substituents on C_2 shows that

– the two methyls on C_2 (one “main-chain” CH_3 at C_1, one branch CH_3) are equivalent to each other,
– the two H’s on C_3 are equivalent,
– the three H’s on the terminal C_4 methyl are equivalent to each other,
– the single H on C_2 is unique.

Hence there are four “types” of H:

A) the six H’s of the two methyls on C_2 (primary)
B) the three H’s of the terminal C_4 methyl (primary)
C) the two H’s on the C_3 methylene (secondary)
D) the one H on the C_2 methine (tertiary)

3. For each type of H, replacing one H by Cl gives one or more products; we must watch for creation of stereocenters.

(i) Type A → substitution on a CH_3 that lies on C_2
Product: CH_3–$C(CH_2Cl)(H)$–CH_2–CH_3 (i.e. a chloromethyl substituent at C_2).
Since it replaces a primary H by Cl, and that carbon (the CH_2Cl) is not stereogenic, we get 1 product.

(ii) Type B → substitution on the terminal C_4 CH_3
Product: CH_3–$CH(CH_3)$–CH_2–CH_2Cl (4-chloro-2-methylbutane).
That carbon is primary, so 1 product.

(iii) Type C → substitution on the CH_2 at C_3
Product: CH_3–$CH(CH_3)$–$CHCl$–CH_3 (3-chloro-2-methylbutane).
Now C_3 becomes CHCl with four different substituents (Cl, H, CH_3, and the $CH(CH_3)_2$ group), so it is a stereocenter. We get two enantiomers.

(iv) Type D → substitution on the CH at C_2
Product: CH_3–$C(Cl)(CH_3)$–CH_2–CH_3 (2-chloro-2-methylbutane).
But C_2 then carries Cl, H was removed, and two identical CH_3 groups—so it is not chiral. Hence 1 product.

4. Count them up:

Type A: 1
Type B: 1
Type C: 2 (enantiomers)

Type D: 1

Total = 1 + 1 + 2 + 1 = 5 distinct chlorination products.

Answer: 5.

79 Problem 79

Which of the following aqueous solution will exhibit highest boiling point?

(1) 0.01 M Urea

(2) 0.01 M KNO_3

(3) 0.01 M Na_2SO_4

(4) 0.015 M $C_6H_{12}O_6$

Hide Solution

Solution:

Here's a detailed, step-by-step solution.

Step 1: Recall the boiling-point elevation formula
The elevation of the boiling point of a solvent by a non-volatile solute is given by

$$\Delta T_b = i\,K_b\,m$$

where
– ΔT_b is the increase in boiling point,

– i is the van 't Hoff factor (number of particles the solute yields in solution),
– K_b is the ebullioscopic constant of the solvent (for water, $K_b = 0.512\ {}^\circ\mathrm{C\,kg/mol}$),
– m is the molality of the solution (mol solute per kg solvent).

For dilute aqueous solutions, molality $m \approx$ molarity M, so we compare $i \times M$ for each.

Step 2: Determine i and compute $i \times M$ for each solution

1. 0.01 M Urea, $CO(NH_2)_2$.
   Urea does not ionize: $i = 1$.

$$iM = 1 \times 0.01 = 0.01.$$

2. 0.01 M KNO_3.
   Potassium nitrate dissociates completely into K^+ and NO_3^-: $i = 2$.

$$iM = 2 \times 0.01 = 0.02.$$

3. 0.01 M Na_2SO_4.
   Sodium sulfate dissociates into 2 Na^+ and SO_4^{2-}: $i = 3$.

$$iM = 3 \times 0.01 = 0.03.$$

4. 0.015 M $C_6H_{12}O_6$ (glucose).
   Glucose does not ionize: $i = 1$.

$$iM = 1 \times 0.015 = 0.015.$$

Step 3: Compare $\Delta T_b \propto iM$
The solution with the largest value of iM will have the greatest boiling-point elevation and hence the highest boiling point. We have:

(1) 0.01
(2) 0.02

(3) 0.03
(4) 0.015

Clearly, the largest is 0.03 for 0.01 M Na_2SO_4.

Answer: the 0.01 M Na_2SO_4 solution exhibits the highest boiling point.

80 Problem 80

Match List - I with List - II List-I A. Haber process B. Wacker oxidation C. Wilkinson catalyst D. Ziegler catalyst List-II I. Fe catalyst II. $PdCl_2$ III. $[(PPh_3)_3RhCl]$ IV. $TiCl_4$ with $Al(CH_3)_3$

(1) A-I, B-II, C-IV, D-III

(2) A-II, B-III, C-I, D-IV

(3) A-I, B-II, C-III, D-IV

(4) A-I, B-IV, C-III, D-II

Hide Solution

Solution:

Here is the detailed matching, step by step, using the required TeX delimiters.

Step 1. Haber process (A)
The Haber process is the synthesis of ammonia:

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

This reaction is carried out over an iron-based catalyst (often Fe promoted with K_2O/Al_2O_3).
⇒ A matches I.

Step 2. Wacker oxidation (B)
The Wacker oxidation converts an alkene into a ketone or aldehyde, e.g.

$$CH_2 = CH_2 + \frac{1}{2}O_2 \xrightarrow{PdCl_2/CuCl_2} CH_3CHO$$

The key catalyst is $PdCl_2$.
⇒ B matches II.

Step 3. Wilkinson's catalyst (C)
Wilkinson's catalyst is the homogeneous hydrogenation catalyst

$$[(PPh_3)_3RhCl]$$

used for alkene hydrogenation.
⇒ C matches III.

Step 4. Ziegler catalyst (D)
Ziegler–Natta catalysts for polyolefin synthesis typically use

$$TiCl_4 \text{ with } Al(CH_3)_3 \,.$$

⇒ D matches IV.

Putting it all together, the correct matching is

A–I,\;B–II,\;C–III,\;D–IV

which corresponds to choice (3).

81 Problem 81

5 moles of liquid X and 10 moles of liquid Y make a solution having a vapour pressure of 70 torr. The vapour pressures of pure X and Y are 63

torr and 78 torr respectively. Which of the following is true regarding the described solution?

(1) The solution shows positive deviation.

(2) The solution shows negative deviation.

(3) The solution is ideal.

(4) The solution has volume greater than the sum of individual volumes.

Hide Solution

Solution:

Here is a step-by-step solution.

1. Compute the mole fractions.
   Let $n_X = 5$, $n_Y = 10$. Then the total number of moles is

$$n_{\text{tot}} = n_X + n_Y = 5 + 10 = 15.$$

   Hence

$$x_X = \frac{n_X}{n_{\text{tot}}} = \frac{5}{15} = \frac{1}{3}, \qquad x_Y = \frac{n_Y}{15} = \frac{10}{15} = \frac{2}{3}.$$

2. Write Raoult's law for an ideal solution.
   If the solution were ideal, its vapour pressure would be

$$P_{\text{ideal}} = x_X\,P_X^0 + x_Y\,P_Y^0 = \frac{1}{3}\cdot 63\;+\;\frac{2}{3}\cdot 78 = 21\;+\;52 = 73\ \text{torr}.$$

3. Compare with the observed vapour pressure.
   We are told the actual vapour pressure is

$$P_{\text{obs}} = 70\ \text{torr}.$$

Since

$$P_{\text{obs}} = 70\ \text{torr} < P_{\text{ideal}} = 73\ \text{torr},$$

the solution's vapour pressure is lower than that predicted by Raoult's law.

4. Interpret the deviation.
   A vapour pressure lower than the ideal value indicates **negative deviation** (stronger X–Y interactions than in the pure components).

Therefore the correct statement is
(2) The solution shows negative deviation.

82 Problem 82

Sugar ' X ' A. is found in honey. B. is a keto sugar. C. exists in α and β - anomeric forms. D. is laevorotatory. ' X ' is :

(1) D-Glucose

(2) D-Fructose

(3) Maltose

(4) Sucrose

Hide Solution

Solution:

Here is a detailed, step-by-step solution:

Step 1: List the four options and their basic types
1. D-Glucose – an aldohexose (an-aldo sugar).
2. D-Fructose – a ketohexose (a keto sugar).
3. Maltose – a disaccharide of two glucose units (α(1→4) link).
4. Sucrose – a disaccharide of glucose and fructose (α(1→2) link), non-reducing.

Step 2: Go through each property A–D

A. “is found in honey.”
Honey is rich in “invert sugar,” which is mainly a mixture of D-glucose and D-fructose.
⇒ Candidates so far: D-Glucose (1) or D-Fructose (2) or Sucrose (4) (since sucrose is hydrolyzed in honey to glucose + fructose), but most free sugar in honey is glucose and fructose.

B. “is a keto sugar.”
A keto sugar has a ketone functional group at C-2.
– D-Glucose (1) is an aldose (aldehyde at C-1).
– D-Fructose (2) is a ketose (ketone at C-2).
– Disaccharides maltose and sucrose are built from mono saccharides; neither “as a whole” is called a keto sugar.
⇒ This singles out D-Fructose (2).

C. “exists in α and β anomeric forms.”
Any free reducing monosaccharide (aldose or ketose) in solution undergoes mutarotation between its α- and β-anomers.

– D-Fructose indeed has α–D-fructofuranose, β–D-fructofuranose (and also pyranose forms).
⇒ D-Fructose satisfies C.

D. “is laevorotatory.”
The “D-”/“L-” system refers to configuration at the highest-numbered chiral carbon; it does not by itself tell you the sign of optical rotation.
– Experimentally, pure D-Glucose is dextrorotatory (d-glucose, $[\alpha]_{naD} \simeq +52°$).
– Pure D-Fructose is laevorotatory (sometimes called “levulose,” $[\alpha]_{naD} \simeq -92°$).
⇒ D-Fructose satisfies D.

Step 3: Conclusion
All four statements A–D hold simultaneously only for **D-Fructose**.

Therefore the correct choice is

$$\boxed{2\ \text{D-Fructose}}.$$

85 Problem 85

The standard heat of formation, in kcal/mol of Ba2+ is : [Given : standard heat of formation of SO4^2- ion (aq) = -216 kcal/mol; standard heat of crystallisation of BaSO4 (s) = -4.5 kcal/mol; standard heat of formation of BaSO4 (s) = -349 kcal/mol]

(1) -128.5

(2) -133.0

(3) +133.0

(4) +220.5

Hide Solution

Solution:

Here is a step-by-step Hess’-law solution.

1. Write down the given standard enthalpies (all in kcal mol⁻¹):

- ΔH°f[SO_4^{2-}(aq)] = –216
- ΔH°f[$BaSO_4$(s)] = –349
- ΔH°cryst for Ba^{2+}(aq) + SO_4^{2-}(aq) → $BaSO_4$(s) = –4.5

2. Note that by definition of heat of crystallization,

$$\Delta H^\circ_{\text{cryst}} = \Delta H^\circ_f\left[\mathrm{BaSO_4(s)}\right] \;-\; \left(\Delta H^\circ_f[\mathrm{Ba^{2+}(aq)}] + \Delta H^\circ_f[\mathrm{SO_4^{2-}(aq)}]\right).$$

3. Denote $x = \Delta H^\circ_f[\mathrm{Ba^{2+}(aq)}]$. Substitute the known values:

$$-4.5 = -349 \;-\; \left(x + (-216)\right) = -349 - x + 216 = -133 - x.$$

4. Solve for x:

$$-4.5 = -133 - x \quad\Longrightarrow\quad x = -(-4.5 + 133) = -128.5\ \mathrm{kcal\,mol^{-1}}.$$

Therefore the standard heat of formation of $\mathrm{Ba^{2+}(aq)}$ is

$$\boxed{-128.5\ \mathrm{kcal\,mol^{-1}}},$$

which corresponds to choice (1).

86 Problem 86

Total number of possible isomers (both structural as well as stereoisomers) of cyclic ethers of molecular formula C4H8O is :

(1) 6

(2) 8

(3) 10

(4) 11

Hide Solution

Solution:

Here is a complete enumeration. We first note that for C_4H_8O

$$\mathrm{DU} = \frac{2C + 2 - H}{2} = \frac{2 \cdot 4 + 2 - 8}{2} = 1$$

so there must be exactly one ring and no π-bonds. The ring must contain the oxygen, and can be of size 3, 4 or 5. We treat each case in turn.

1. Three-membered cyclic ethers (oxiranes, “epoxides”)

In an unsubstituted oxirane the formula is C_2H_4O, so we need two extra carbons as substituents. Two logical distributions of the 2C among substituents are:

a) One ethyl substituent
– Structure: 1-ethyloxirane
– That carbon (call it C^1) has substituents O, C^2, Et and H → one stereocenter → 2

enantiomers.

b) Two methyl substituents
i) Both on the same carbon → 1,1-dimethyloxirane
– That carbon has two identical Me groups → no stereocenter → 1 isomer
ii) One on each carbon → 1,2-dimethyloxirane
– Two stereocenters (one at each ring carbon) → cis vs. trans
• cis isomer is meso (it has a mirror plane) → 1
• trans isomer is chiral → a pair of enantiomers → 2
⇒ total for 1,2-dimethyl = 3

Summing up for the epoxides:

$$\text{1-ethyloxirane}:\ 2 \quad + \quad \text{1,1-dimethyloxirane}:\ 1 \quad + \quad \text{1,2-dimethyloxirane}:$$

2. Four-membered cyclic ethers (oxetanes)

Unsubstituted oxetane is C_3H_6O; we need one extra C as a methyl substituent. Label the ring O–C^2–C^3–C^4. By symmetry $C^2 \equiv C^4$, so there are two distinct monosubstituted oxetanes:

a) 2-Methyloxetane
– The substituted carbon is CH (Me, H, O, other C) → stereocenter → 2 enantiomers.

b) 3-Methyloxetane
– That carbon is CH(Me, H, paths via C^2 or C^4)—because of the remaining mirror plane it is achiral → 1 isomer.

Total for oxetanes: 2 + 1 = 3.

3. Five-membered cyclic ether

This is just tetrahydrofuran (C_4H_8O), unsubstituted. No stereocenters → 1 isomer.

Finally, adding all three classes:

epoxides (6) + oxetanes (3) + tetrahydrofuran (1) = 10

Answer: there are 10 possible cyclic-ether isomers of C_4H_8O.

87 Problem 87

Identify the correct orders against the property mentioned A. H2O > NH3 > CHCl3 - dipole moment B. XeF4 > XeO3 > XeF2 - number of lone pairs on central atom C. O-H > C-H > N-H - bond length D. N2 > O2 > H2 - bond enthalpy Choose the correct answer from the options given below :

(1) A, D only

(2) B, D only

(3) A, C only

(4) B, C only

Hide Solution

Solution:

Solution:

We examine each statement (A–D) by comparing the given property values and then decide which orders are correct.

1. Statement A: Dipole moments
   Given order:

$$H_2O > NH_3 > CHCl_3$$

Actual dipole moments (in Debye, D) are approximately

$$\mu(H_2O) \approx 1.85\,\mathrm{D}, \quad \mu(\mathrm{NH_3}) \approx 1.47\,\mathrm{D}, \quad \mu(\mathrm{CHCl_3}) \approx 1.04\,\mathrm{D}.$$

Hence the correct descending order is indeed

$$1.85 > 1.47 > 1.04 \quad \Longrightarrow \quad H_2O > NH_3 > CHCl_3.$$

⇒ Statement A is **correct**.

2. Statement B: Number of lone pairs on the central atom
   - In XeF_4, Xe has 4 bonds → uses 4 of its 8 valence electrons → leaves 4 e^- (=2 lone pairs).
   - In XeO_3, Xe has 3 bonds → leaves 2 e^- (=1 lone pair).
   - In XeF_2, Xe has 2 bonds → leaves 6 e^- (=3 lone pairs).

   Thus the actual number of lone pairs is

$$XeF_2 : 3, \quad XeF_4 : 2, \quad XeO_3 : 1,$$

so the correct descending order is

$$XeF_2 > XeF_4 > XeO_3,$$

not the given $XeF_4 > XeO_3 > XeF_2$.
⇒ Statement B is **incorrect**.

3. Statement C: Bond lengths
   Typical single-bond lengths (in ångström, Å) are

$$O\text{–}H \approx 0.96\ \text{Å}, \quad N\text{–}H \approx 1.01\ \text{Å}, \quad C\text{–}H \approx 1.09\ \text{Å}.$$

Thus the true order (shortest → longest) is

$$O\text{–}H < N\text{–}H < C\text{–}H,$$

whereas the statement claims $O\text{–}H > C\text{–}H > N\text{–}H$, which is reversed.
⇒ Statement C is **incorrect**.

4. Statement D: Bond enthalpies
Approximate bond dissociation enthalpies (kJ·mol^{-1}) are

$$N \equiv N \approx 945, \quad O = O \approx 498, \quad H\text{–}H \approx 436.$$

Hence the descending order is

$$945 > 498 > 436 \quad \Longrightarrow \quad N_2 > O_2 > H_2.$$

⇒ Statement D is **correct**.

Since only A and D are correct, the answer is
Option (1): A and D only.

88 Problem 88

Higher yield of NO in N2 (g) + O2 (g) ⇌ 2 NO (g) [ΔH of the reaction = +180.7 kJ mol^-1] can be obtained at A. higher temperature B. lower temperature C. higher concentration of N2 D. higher concentration of O2 Choose the correct answer from the options given below:

(1) A, D only

(2) B, C only

(3) B, C, D only

(4) A, C, D only

Hide Solution

Solution:

Here is a step-by-step Le Châtelier's-principle analysis of the given reaction:

$N_2(g) + O_2(g) \rightleftharpoons 2\ NO(g)$ $\Delta H = +180.7\ kJ \cdot mol^{-1}$

1. Identify the thermochemical character

Since ΔH is positive, the forward reaction is **endothermic**. In other words, heat may be thought of as a "reactant":

$$\mathrm{N_2 + O_2 + heat \longrightarrow 2\,NO}\,.$$

2. Effect of changing temperature

– Raising the temperature adds "heat" to the system. By Le Châtelier's principle, the equilibrium shifts to consume that added heat, i.e. toward the **endothermic** (forward) direction, producing more NO.

– Lowering the temperature would remove heat and shift the equilibrium toward the exothermic (reverse) direction, producing less NO.

⇒ **Higher temperature (A)** favors NO formation; **lower temperature (B)** does not.

3. Effect of changing concentrations of reactants

– Increasing $[N_2]$ disturbs the equilibrium; the system shifts to the right to consume extra N_2, forming more NO.

– Similarly, increasing $[O_2]$ shifts the equilibrium to the right to consume the added O_2, also yielding more NO.

⇒ **Higher $[N_2]$ (C)** and **higher $[O_2]$ (D)** both increase the yield of NO.

4. Summary of favorable conditions for maximum NO yield

A. higher temperature ✔

B. lower temperature ✘

C. higher $[N_2]$ ✔

D. higher $[O_2]$ ✔

5. Choose the correct option
   Only A, C and D are correct ⇒ option (4).

Answer: **(4) A, C, D only**.

89 Problem 89

If the rate constant of a reaction is 0.03 s^-1, how much time does it take for 7.2 mol L^-1 concentration of the reactant to get reduced to 0.9 mol L^-1? (Given: log 2 = 0.301)

(1) 69.3 s

(2) 23.1 s

(3) 210 s

(4) 21.0 s

Hide Solution

Solution:

Here the reaction is first-order, so the integrated rate law is

$$\ln \frac{[A]_0}{[A]} = k\,t.$$

We are given

$$k = 0.03\ \mathrm{s}^{-1}, \quad [A]_0 = 7.2\ \mathrm{mol{\cdot}L}^{-1}, \quad [A] = 0.9\ \mathrm{mol{\cdot}L}^{-1}.$$

Step 1. Compute the concentration ratio:

$$\frac{[A]_0}{[A]} = \frac{7.2}{0.9} = 8.$$

Step 2. Solve for t:

$$t = \frac{1}{k} \ln \frac{[A]_0}{[A]} = \frac{1}{0.03} \ln(8).$$

Step 3. Evaluate $\ln(8)$ using $\ln x = 2.303\ \log_{10} x$ and $\log_{10} 2 = 0.301$:

$$\log_{10}(8) = \log_{10}(2^3) = 3\ \log_{10} 2 = 3 \times 0.301 = 0.903,$$

$$\ln(8) = 2.303 \times 0.903 \approx 2.0796.$$

Step 4. Plug in:

$$t = \frac{2.0796}{0.03} \approx 69.32\ \mathrm{s}.$$

Rounded to three-significant-figure accuracy, $t = 69.3$ s.

Answer: (1) 69.3 s.

90 Problem 90

Which one of the following reactions does NOT belong to "Lassaigne's test"?

(1) Na + C + N →Δ NaCN

(2) 2 Na + S →Δ Na2S

(3) Na + X →Δ NaX

(4) 2 CuO + C →Δ 2 Cu + CO2

Hide Solution

Solution:

Here’s a step-by-step analysis.

1. What is Lassaigne’s (sodium-fusion) test?
Organic compounds often contain heteroatoms (N, S, halogens). In the sodium-fusion test, a small piece of sodium metal is fused with the sample; this converts
– nitrogen into sodium cyanide (NaCN),
– sulfur into sodium sulfide ($\mathrm{Na_2S}$),
– halogens into sodium halide (NaX).

After fusion, the mixture is extracted with water and the filtrate is tested for $\mathrm{CN^-}$, $\mathrm{S^{2-}}$ or $\mathrm{X^-}$ by appropriate reagents.

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2. Examine each given reaction

(1) $\mathrm{Na + C + N \xrightarrow{\Delta} NaCN}$

- This is exactly how nitrogen in an organic sample is converted into CN^- (via NaCN).

(2) $2\,\mathrm{Na} + \mathrm{S} \xrightarrow{\Delta} \mathrm{Na_2S}$
- Sulfur in the sample is converted to S^{2-} (via $\mathrm{Na_2S}$).

(3) $\mathrm{Na} + \mathrm{X} \xrightarrow{\Delta} \mathrm{NaX}$
- A halogen atom X in the sample is converted to X^- (via NaX).

(4) $2\,\mathrm{CuO} + \mathrm{C} \xrightarrow{\Delta} 2\,\mathrm{Cu} + \mathrm{CO_2}$
- This is simply the reduction of copper(II) oxide by carbon to give copper metal and carbon dioxide.
- **It has nothing to do with sodium fusion or detection of N, S or halogens.**

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3. Conclusion
The reaction that does _not_ belong to Lassaigne’s (sodium-fusion) test is option **(4)**.

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