FINAL EXAM

PRACTICE PROBLEMS: SOLUTIONS

CHEMISTRY 165B // SPRING 2020

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TABLE OF CONTENTS

(1) KINETICS
(2) EQUILIBRIUM
(3) ACID-BASE
(4) THERMODYNAMICS
(5) ELECTROCHEMISTRY
(6) NUCLEAR CHEMISTRY
(7) ORGANIC CHEMISTRY
(8) BIOCHEMISTRY
(9) TRANSITION METALS

KINETICS: PROBLEM 1.1

Consider the reaction between nitrogen monoxide and hydrogen gases:

$$2\ NO\ (g) + 2\ H_2\ (g) \rightarrow N_2\ (g) + 2\ H_2O\ (g)$$

Given the following initial rates data collected at 300 K, determine the rate law for the reaction.

Expt.	$[NO]_0$ (M)	$[H_2]_0$ (M)	Initial Rate (M/min)
1	0.0060	0.0010	1.8×10^{-4}
2	0.0060	0.0020	3.6×10^{-4}
3	0.0010	0.0060	3.0×10^{-5}
4	0.0020	0.0060	1.2×10^{-4}

— answer —

Begin by constructing the generic rate law: $\text{Rate} = k[\text{NO}]^a[\text{H}_2]^b$

Understand that we will need to solve for the orders *a* and *b* using the isolation method.

Compare experiments 3 and 4 for order a:

$$\frac{\text{Rate}_4}{\text{Rate}_3} = \frac{k[\text{NO}]_4^a[\text{H}_2]_4^b}{k[\text{NO}]_3^a[\text{H}_2]_3^b} \quad ;\ k[\text{H}_2]^b \text{ cancels}$$

$$\frac{\text{Rate}_4}{\text{Rate}_3} = \left(\frac{[\text{NO}]_4}{[\text{NO}]_3}\right)^a$$

$$\frac{1.2 \times 10^{-4}\ \text{M/min}}{3.0 \times 10^{-5}\ \text{M/min}} = \left(\frac{0.0020\ \text{M}}{0.0010\ \text{M}}\right)^a$$

$$4 = 2^a$$

$$a = 2$$

Compare experiments 2 and 1 for order b:

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[\text{NO}]_2^a[\text{H}_2]_2^b}{k[\text{NO}]_1^a[\text{H}_2]_1^b} \quad ;\ k[\text{NO}]^a \text{ cancels}$$

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \left(\frac{[\text{H}_2]_2}{[\text{H}_2]_1}\right)^b$$

$$\frac{3.6 \times 10^{-4}\ \text{M/min}}{1.8 \times 10^{-4}\ \text{M/min}} = \left(\frac{0.0020\ \text{M}}{0.0010\ \text{M}}\right)^b$$

$$2 = 2^b$$

$$b = 1$$

This means that our rate law is: $\text{Rate} = k[\text{NO}]^2[\text{H}_2]^1$

KINETICS: PROBLEM 1.2

Consider the reaction between nitrogen monoxide and hydrogen gases:

$$2\ NO\ (g) + 2\ H_2\ (g) \rightarrow N_2\ (g) + 2\ H_2O\ (g)$$

Given the following initial rates data collected at 300 K, determine the rate constant *k* (value and units) for the reaction.

Expt.	$[NO]_0$ (M)	$[H_2]_0$ (M)	Initial Rate (M/min)
1	0.0060	0.0010	1.8×10^{-4}
2	0.0060	0.0020	3.6×10^{-4}
3	0.0010	0.0060	3.0×10^{-5}
4	0.0020	0.0060	1.2×10^{-4}

— answer —

From the previous slide, our rate law is: $\text{Rate} = k[\text{NO}]^2[\text{H}_2]^1$

Now that we have our rate law, we can solve for the rate constant, *k*, by plugging in the values from any experiment.

I'll use experiment 1:

$$\text{Rate}_1 = k[\text{NO}]_1^2[\text{H}_2]_1^1$$

$$1.8 \times 10^{-4}\ \frac{\text{M}}{\text{min}} = k(0.0060\ \text{M})^2(0.0010\ \text{M})$$

$$k = 5.0 \times 10^3\ \text{M}^{-2} \cdot \text{min}^{-1}$$

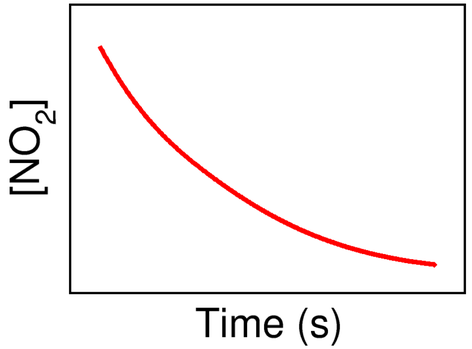
KINETICS: PROBLEM 1.3

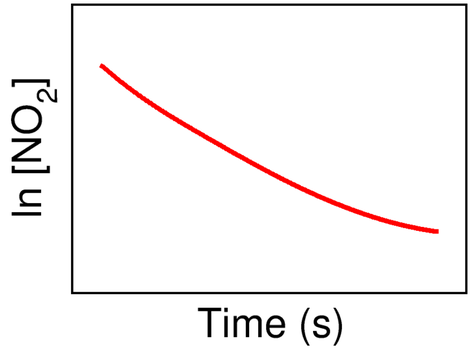
The following concentration-time data are plotted below for the decomposition of nitrogen dioxide gas at 298 K.

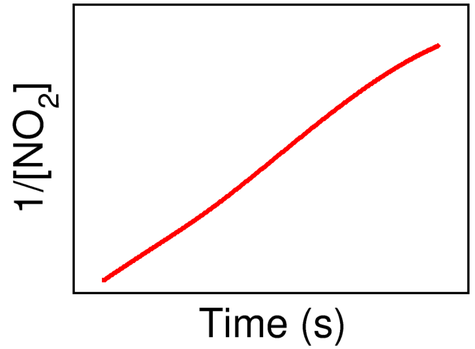
$$2\ NO_2\ (g) \rightarrow 2\ NO\ (g) + O_2\ (g)$$

What is the order of the reaction with respect to $[NO_2]$?

Time (s)	$[NO_2]$ (M)
10.	0.0044
26.	0.0034
44.	0.0027
70.	0.0020
120.	0.0014







— answer —

Recall that the concentration-time plot that gives a straight line ($y = mx + b$) gives us the order of the reaction.

- If $[NO_2]$ vs. time is a linear plot, then the reaction is zero-order with respect to $[NO_2]$.
- If ln $[NO_2]$ vs. time is a linear plot, then the reaction is first-order with respect to $[NO_2]$.
- If $1/[NO_2]$ vs. time is a linear plot, then the reaction is second-order with respect to $[NO_2]$.

KINETICS: PROBLEM 1.4

Consider the decomposition of NO_2 (g) from Problem 1.3:

$$2\ NO_2\ (g) \rightarrow 2\ NO\ (g) + O_2\ (g)$$

Which of the following proposed mechanism(s) is (are) not valid?

Justify your choice briefly.

– answer –

From the previous slides, our rate law is: $\text{Rate} = k[NO_2]^2$

(i)
$NO_2 \rightarrow NO + O$ (slow)
$NO_2 + O \rightarrow NO + O_2$ (fast)

(ii)
$NO_2 + NO_2 \rightleftharpoons N_2O_4$ (fast)
$N_2O_4 \rightarrow NO + NO_3$ (slow)
$NO_3 \rightarrow NO + O_2$ (fast)

(iii)
$NO_2 + NO_2 \rightarrow NO + NO_3$ (slow)
$NO_3 \rightarrow NO + O_2$ (fast)

To find a valid mechanism, we need the elementary rate law for the slowest elementary step to match the overall rate law.

Mechanism (i)			Elementary rate laws
Step 1:	$NO_2 \rightarrow NO + O$	(slow)	$\text{rate}_1 = k_1[NO_2]$
Step 2:	$N_2O + O \rightarrow N_2 + O_2$	(fast)	

Mechanism (ii)			Elementary rate laws
Step 1:	$NO_2 + NO_2 \rightleftharpoons N_2O_4$	(fast)	$K_c = \frac{[N_2O_4]}{[NO_2]^2} \Longrightarrow [N_2O_4] = K_c[NO_2]^2$
Step 2:	$N_2O_4 \rightarrow NO + NO_3$	(slow)	$\text{rate}_2 = k_2[N_2O_4] = k_2K_c[NO_2]^2 = k'[NO_2]^2$
Step 3:	$NO_3 \rightarrow NO + O_2$	(fast)	

Mechanism (iii)			Elementary rate laws
Step 1:	$NO_2 + NO_2 \rightarrow NO + NO_3$	(slow)	$\text{rate}_1 = k_1[NO_2]^2$
Step 2:	$NO_3 \rightarrow NO + O_2$	(fast)	

Mechanism (i) is not valid since it is first-order in $[NO_2]$.

Some notes about rate laws:

- We can write elementary rate laws based on the stoichiometry of the elementary steps.
- The rate laws can only depend on reactants, not products or intermediates.
- If an intermediate is present in the elementary rate law, it must be re-expressed in terms of reactants somehow – see Mechanism (ii).
- If a prior step is in equilibrium, the reactant or product concentrations can be expressed in terms of the K_c expression – see Mechanism (ii).

KINETICS: PROBLEM 1.5

Consider the decomposition of NO_2 (g) from Problem 1.3 and 1.4: $2\ NO_2\ (g) \rightarrow 2\ NO\ (g) + O_2\ (g)$

The initial concentration of $[NO_2]_0 = 5.56 \times 10^{-3}$ M. After 500 s have elapsed, the concentration of NO_2 is 4.14×10^{-4} M.

Calculate the rate constant *k* (value and units) for the reaction.

– answer –

From the previous slides, our rate law is: $\text{Rate} = k[NO_2]^2$

We can use the second-order integrated rate law to determine the value of the rate constant *k*:

$$\frac{1}{[NO_2]_t} = kt + \frac{1}{[NO_2]_0}$$

$$\frac{1}{4.14 \times 10^{-4}\ \text{M}} = k(500\ \text{s}) + \frac{1}{5.56 \times 10^{-3}\ \text{M}}$$

$$k = 4.47\ \text{M}^{-1} \cdot \text{s}^{-1}$$

EQUILIBRIUM: PROBLEM 2.1

Consider the following gaseous equilibrium: $2\ H_2S\ (g) \rightleftharpoons 2\ H_2\ (g) + S_2\ (g)$

A 10.0 L vessel contains 10.0 atm of H_2S gas at 800 K initially. If the partial pressure of S_2 gas is 0.020 atm at equilibrium, what is the value of K_c?

– answer –

Step 1: Write down the expression for the equilibrium constant, K_p.

Step 2: Prepare an ICE chart (Initial, Change, and Equilibrium)

Step 3: Recognize that $x = P_{S_2} = 0.020\ \text{atm}$

Step 4: Solve for the equilibrium partial pressures.

Step 5: Use the Equilibrium (E) values to evaluate K_p.

Step 6: Solve for K_c.

	$2\ H_2S$	$\rightleftharpoons$	$2\ H_2$	+	S_2
I	10.0 atm		0 atm		0 atm
C	– 2x		+ 2x		+ x
E	10.0 – 2x		2x		x

$$P_{S_2} = 0.020\ \text{atm}$$
$$P_{H_2} = 2(0.020\ \text{atm}) = 0.040\ \text{atm}$$
$$P_{H_2S} = (10.0 - 2{\times}0.020)\ \text{atm} = 9.9_6\ \text{atm}$$

Note that $\Delta n = \Sigma n_{prod} - \Sigma n_{react} = 3 - 2 = 1$

$$K_p = \frac{(P_{H_2})^2 P_{S_2}}{(P_{H_2S})^2}$$

$$= \frac{(0.040)^2(0.020)}{(9.9_6)^2}$$

$$K_p = 3.2_3 \times 10^{-7}$$

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

$$3.2_3 \times 10^{-7} = K_c(0.08206 \times 800)^{3-2}$$

$$K_c = 4.9 \times 10^{-9}$$

EQUILIBRIUM: PROBLEM 2.2

Which of the following changes would increase the concentration of $[H_2]$ in the following chemical equilibrium?

$$C\,(s) + H_2O\,(g) \rightleftharpoons CO\,(g) + H_2\,(g) \qquad ; \Delta H = +131\ kJ$$

— answer —

Write down the expressions for the equilibrium constants: $K_c = \dfrac{[CO][H_2]}{[H_2O]}$ $K_p = \dfrac{P_{CO}P_{H_2}}{P_{H_2O}}$

	Change	Response of system	$[H_2]$
(a)	Adding more C (s).	Since pure solids/liquids do not affect equilibria, there will be no shift.	No change
(b)	Adding more CO (g).	Adding products will make $Q > K$, and the system will shift to the left to achieve equilibrium.	Decrease
(c)	Removing H_2O (g).	Removing reactants will make $Q > K$, and the system will shift to the left to achieve equilibrium.	Decrease
(d)	Increasing the pressure on the system by reducing the volume.	Increasing the total pressure of the system increases the partial pressures of the gases. As such, the system will shift to the side with a lesser number of moles of gas (left) in order to decrease the partial pressures and total pressure of the system.	Decrease
(e)	Increasing the temperature.	Since the reaction is endothermic ($\Delta H > 0$), we can treat heat as a reactant. heat + C (s) + H_2O (g) ⇌ CO (g) + H_2 (g) Increasing temperature/heat would shift the reaction to the right ($Q < K$).	Increase

ACID-BASE: PROBLEM 3.1

Benzoic acid (C_6H_5COOH) is a weak acid with a $K_a = 6.25 \times 10^{-5}$ at 298 K.

What is the pH of a 125 mL solution of 0.10 M C_6H_5COOH?

— answer —

Step 1: Note that C_6H_5COOH is a weak acid because K_a is small, so we have to consider the weak acid dissociation equilibrium.

Step 2: Write out the balanced equilibrium for the weak acid dissociation and the K_a expression.

Step 3: Construct an ICE chart. Fill in the initial values, then the stoichiometric changes (x), and then equilibrium concentrations.

Step 4: We can use the equilibrium (E) concentration values to plug into our expression for K_a.

Step 5: Finally solve for x. What does x represent?

Step 6: Calculate the pH.

	C_6H_5COOH	$\rightleftharpoons$	H^+	+	$C_6H_5COO^-$
I	0.10 M		0		0
C	− x		+ x		+ x
E	0.10 − x		x		x

Because the value of K_a is very small, we know that the system will undergo very little change (x value) toward the right in order to achieve equilibrium. In other words, we can take "x" to be very small/negligible and invoke the approximation that:

$0.10 - x \approx 0.10$

$$K_a = \frac{[H^+][C_6H_5COO^-]}{[C_6H_5COOH]} = 6.25 \times 10^{-5}$$

$$6.25 \times 10^{-5} = \frac{(x)(x)}{0.10 - x}$$

$$6.25 \times 10^{-5} \approx \frac{x^2}{0.10}$$

$$x = 2.5 \times 10^{-3}\ \text{M} = [H^+]$$

$$\text{pH} = -\log(2.5 \times 10^{-3}) = 2.60$$

ACID-BASE: PROBLEM 3.2

Hydrazoic acid (N_3H) is a weak acid with a $K_a = 1.9 \times 10^{-5}$ at 298 K.

To 100. mL of 0.25 M N_3H we add 0.50 g of NaOH. What is the pH of the resulting solution?

You may assume no change in volume or temperature.

— answer —

Because NaOH is a strong base it dissociates completely: NaOH (s) → Na^+ (aq) + OH^- (aq)

Step 1: Determine the number of moles of N_3H and OH^-:

$$n_{N_3H} = 0.100\ \text{L} \times \frac{0.25\ \text{mol}\ N_3H}{1\ \text{L}} = 0.025\ \text{mol}\ N_3H \qquad n_{OH^-} = 0.50\ \text{g NaOH} \times \frac{1\ \text{mol NaOH}}{39.998\ \text{g}} \times \frac{1\ \text{mol}\ OH^-}{1\ \text{mol NaOH}} = 0.012_5\ \text{mol}\ OH^-$$

Step 2: Consider the reaction (not equilibrium) between N_3H and OH^-.

Step 3: Note we are not at the equivalence point, so we can use the Henderson-Hasselbach equation to find the pH.

	N_3H	+	OH^-	→	N_3^-	+	H_2O
I	0.025 mol		0.012_5 mol		0 mol		n/a
C	$-\ 0.012_5$		$-\ 0.012_5$		$+\ 0.012_5$		n/a
F	0.012_5		0		0.012_5		n/a
	0.12_5 M		0 M		0.12_5 M		n/a

OH^- is the limiting reactant.

Convert to M by dividing by V_{tot} = 0.100 L

$$\text{pH} = \text{p}K_a + \log\frac{[N_3^-]}{[N_3H]}$$

$$= -\log(1.9 \times 10^{-5}) + \log\frac{[0.12_5]}{[0.12_5]}$$

$$= 4.72_1 - 0$$

$$\text{pH} = 4.72$$

ACID-BASE: PROBLEM 3.3

A buffer with pH = 4.87 is made from 10.0 mL of 0.75 M acetic acid (CH_3COOH) and 5.0 mL of 2.0 M sodium acetate ($NaCH_3COO$). Acetic acid is a weak acid with a $K_a = 1.8 \times 10^{-5}$ at 298 K.

Calculate the pH of the solution if 0.00010 mol of NaOH are added to the buffer.

You may assume no change in volume or temperature.

— answer —

First, ask yourself what NaOH will react with in the buffer equilibrium: the acid or its conjugate-base?

Since NaOH is a base, it should react with the acid (not equilibrium) via: $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

We can construct an IC"E" chart in moles to help us out here.

	CH_3COOH	+	OH^-	→	CH_3COO^-	+	H_2O
I	0.0075 mol		0.00010 mol		0.010 mol		*n/a*
C	– 0.00010		– 0.00010		+ 0.00010		*n/a*
F	0.0074		0		0.010_1		*n/a*

Why ICF and not ICE?
Remember that ICE charts are for equilibrium processes. At the instant of mixing HCl into the buffer, we get a non-equilibrium and unidirectional reaction between the conjugate-base and H^+ to form acid. The "ICE" chart setup is still *useful* because it simplifies the stoichiometry calculations we would normally have to do for non-equilibrium chemical reactions: (1) find the limiting reactant, (2) determine how much excess reactant is left, and (3) determine how much product is formed.

Now, just apply the Henderson-Hasselbach equation to estimate the pH:

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$

$$= -\log(1.8 \times 10^{-5}) + \log\left(\frac{\frac{0.010_1 \text{ mol}}{0.0150 \text{ L}}}{\frac{0.0074 \text{ mol}}{0.0150 \text{ L}}}\right)$$

$$= 4.74_5 + 0.13_5$$

$$\mathrm{pH} = 4.88$$

THERMODYNAMICS: PROBLEM 4.1

Consider the following reaction:

$$CaSO_4{\cdot}2H_2O\ (s) \rightarrow CaSO_4\ (s) + 2\ H_2O\ (g)$$

Given the following thermodynamic data at 25 °C, calculate the standard Gibbs free energy change (ΔG°_{rxn}) at 25 ° C.

	$CaSO_4{\cdot}2H_2O$ (s)	$CaSO_4$ (s)	H_2O (g)
$\Delta G^\circ_f \left(\frac{kJ}{mol}\right)$	−1797.4	−1322.0	−228.6
$\Delta H^\circ_f \left(\frac{kJ}{mol}\right)$	−2022.6	−1434.5	−241.8
$S^\circ \left(\frac{J}{mol \cdot K}\right)$	194.1	106.5	188.8

— answer —

There are two ways to find the value of ΔG°_{rxn}:

(1)
$$\Delta G^\circ_{rxn} = \sum n_{prod}\,\Delta G^\circ_{f,prod} - \sum n_{react}\,\Delta G^\circ_{f,react}$$

$$= \left[(1\ mol\ CaSO_4)\times\left(-1322.0\,\frac{kJ}{mol}\right) + (2\ mol\ H_2O)\times\left(-228.6\,\frac{kJ}{mol}\right)\right] - (1\ mol\ CaSO_4\cdot 2H_2O)\times\left(-1797.4\,\frac{kJ}{mol}\right)$$

$$\Delta G^\circ_{rxn} = 18.2\ kJ$$

(2)
$$\Delta H^\circ_{rxn} = \left[(1\ mol\ CaSO_4)\times\left(-1434.5\,\frac{kJ}{mol}\right) + (2\ mol\ H_2O)\times\left(-241.8\,\frac{kJ}{mol}\right)\right] - (1\ mol\ CaSO_4\cdot 2H_2O)\times\left(-2022.6\,\frac{kJ}{mol}\right) = 104.5\ kJ$$

$$\Delta S^\circ_{rxn} = \left[(1\ mol\ CaSO_4)\times\left(106.5\,\frac{J}{mol\cdot K}\right) + (2\ mol\ H_2O)\times\left(188.8\,\frac{J}{mol\cdot K}\right)\right] - (1\ mol\ CaSO_4\cdot 2H_2O)\times\left(194.1\,\frac{J}{mol\cdot K}\right) = 290.0\,\frac{J}{K}$$

$$\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn} = 104.5\ kJ - (298.15\ K)\left(0.2900\,\frac{kJ}{K}\right) = 18.0\ kJ$$

THERMODYNAMICS: PROBLEM 4.2

Consider the following decomposition reaction:

$$2\ \text{HgO (s)} \rightarrow 2\ \text{Hg (l)} + \text{O}_2\ \text{(g)}$$

Given the following thermodynamic data at 25 °C, determine if the decomposition reaction is spontaneous at 800 K.

	HgO (s)	Hg (l)	O_2 (g)
$\Delta G_f^o \left(\frac{\text{kJ}}{\text{mol}}\right)$	–58.5	0	0
$\Delta H_f^o \left(\frac{\text{kJ}}{\text{mol}}\right)$	–90.83	0	0
$S° \left(\frac{\text{J}}{\text{mol} \cdot \text{K}}\right)$	70.29	75.9	205.0

– answer –

There are two ways to solve this problem. For both, you will need to first find the following two properties:

$$\Delta H_{\text{rxn}}^{\text{o}} = \left[(2\ \text{mol Hg}) \times \left(0 \frac{\text{kJ}}{\text{mol}}\right) + (1\ \text{mol O}_2) \times \left(0 \frac{\text{kJ}}{\text{mol}}\right)\right] - (2\ \text{mol HgO}) \times \left(-58.5 \frac{\text{kJ}}{\text{mol}}\right) = 181.66\ \text{kJ}$$

$$\Delta S_{\text{rxn}}^{\text{o}} = \left[(2\ \text{mol Hg}) \times \left(75.0 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right) + (1\ \text{mol O}_2) \times \left(205.0 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right)\right] - (2\ \text{mol HgO}) \times \left(70.29 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right) = 216.42\ \frac{\text{J}}{\text{K}}$$

Method 1: Calculate ΔG_{rxn}^o at 800 K

$$\Delta G_{\text{rxn}}^{\text{o}} = \Delta H_{\text{rxn}}^{\text{o}} - T\Delta S_{\text{rxn}}^{\text{o}} = 181.66\ \text{kJ} - (800\ \text{K}) \left(0.21642\ \frac{\text{kJ}}{\text{K}}\right) = 8.68\ \text{kJ}$$

Method 2: Calculate the T at which the reaction would be spontaneous

$$0 = \Delta H_{\text{rxn}}^{\text{o}} - T\Delta S_{\text{rxn}}^{\text{o}}$$

$$T = \frac{\Delta H_{\text{rxn}}^{\text{o}}}{\Delta S_{\text{rxn}}^{\text{o}}} = \frac{181.66\ \text{kJ}}{0.21642\ \frac{\text{kJ}}{\text{K}}} = 839\ \text{K}$$

Either method shows that the reaction is nonspontaneous at 800 K.

ELECTROCHEMISTRY: PROBLEM 5.1

Using the following table of standard reduction potentials, which of the following redox reactions represent spontaneous reactions taking place in a voltaic/Galvanic cell?

Half-reaction	$E°$ (V)
$Ag^+ (aq) + e^- \rightarrow Ag (s)$	+0.800
$Sn^{2+} (aq) + 2\ e^- \rightarrow Sn (s)$	−0.136
$Ni^{2+} (aq) + 2\ e^- \rightarrow Ni (s)$	−0.257
$Mn^{2+} (aq) + 2\ e^- \rightarrow Mn (s)$	−1.185
$Al^{3+} (aq) + 3\ e^- \rightarrow Al (s)$	−1.662
$Na^+ (aq) + e^- \rightarrow Na (s)$	−2.710

— answer —

Each of the redox reactions uses the same reducing agent (anode): $Mn (s) \rightarrow Mn^{2+} (aq) + 2\ e^-$ with $E° = -1.185\ \text{V}$.

A spontaneous (voltaic cell) reaction will have: $E^{\text{o}}_{\text{cell}} = E^{\text{o}}_{\text{cathode}} - E^{\text{o}}_{\text{anode}} > 0$ or $E^{\text{o}}_{\text{cathode}} > E^{\text{o}}_{\text{anode}}$.

	Redox Reaction		Spontaneous?
(a)	$Mn (s) + Sn^{2+} (aq) \rightarrow Mn^{2+} (aq) + Sn (s)$	$E^{\text{o}}_{\text{cell}} = -0.136\ \text{V} - (-1.185\ \text{V}) = +1.049\ \text{V}$	Yes
(b)	$Mn (s) + Ni^{2+} (aq) \rightarrow Mn^{2+} (aq) + Ni (s)$	$E^{\text{o}}_{\text{cell}} = -0.257\ \text{V} - (-1.185\ \text{V}) = +0.928\ \text{V}$	Yes
(c)	$Mn (s) + 2\ Na^+ (aq) \rightarrow Mn^{2+} (aq) + 2\ Na (s)$	$E^{\text{o}}_{\text{cell}} = -2.710\ \text{V} - (-1.185\ \text{V}) = -1.525\ \text{V}$	No
(d)	$3\ Mn (s) + 2\ Al^{3+} (aq) \rightarrow 3\ Mn^{2+} (aq) + 2\ Al (s)$	$E^{\text{o}}_{\text{cell}} = -1.662\ \text{V} - (-1.185\ \text{V}) = -0.477\ \text{V}$	No
(e)	$Mn (s) + 2\ Ag^+ (aq) \rightarrow 3\ Mn^{2+} (aq) + 2\ Ag (s)$	$E^{\text{o}}_{\text{cell}} = +0.800\ \text{V} - (-1.185\ \text{V}) = +1.985\ \text{V}$	Yes

ELECTROCHEMISTRY: PROBLEM 5.2

A voltaic/Galvanic cell is made from a compartment with 1.20 M $Fe(NO_3)_3$ and 1.10 M $Fe(NO_3)_2$, a compartment with 0.95 M $Cr(NO_3)_2$ and 1.00 M $Cr(NO_3)_3$, both at 25 °C, connected by a wire, salt bridge, and two platinum electrodes. Calculate the initial potential of this cell.

Half-reaction	$E°$ (V)
Fe^{3+} (aq) + e^- → Fe^{2+} (aq)	+0.770
Cr^{3+} (aq) + e^- → Cr^{2+} (aq)	–0.410
Fe^{2+} (aq) + 2 e^- → Fe (s)	–0.447
Cr^{3+} (aq) + 3 e^- → Cr (s)	–0.740

– answer –

First, consider the two aqueous metal cations that exist in each compartment: Fe^{3+} (aq), Fe^{2+} (aq) and Cr^{2+} (aq), Cr^{3+} (aq)

Second, write the net ionic equation for the spontaneous redox reaction that would take place between these ions:

Cathode (Reduction):	Fe^{3+} (aq)	+	e^-	→	Fe^{2+} (aq)			
Anode (Oxidation):			Cr^{2+} (aq)	→	Cr^{3+} (aq)	+	e^-	
Cell	Fe^{3+} (aq)	+	Cr^{2+} (aq)	→	Fe^{2+} (aq)	+	Cr^{3+} (aq)	

$$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$$
$$= +0.770\ \text{V} - (-0.410\ \text{V})$$
$$E^{o}_{cell} = +1.180\ \text{V}$$

Now, we can apply the Nernst equation find the nonstandard initial cell potential, keeping in mind the form of Q.

$$E_{cell} = E^{o}_{cell} - \frac{RT}{nF}\ln\frac{[Fe^{2+}][Cr^{3+}]}{[Fe^{3+}][Cr^{2+}]}$$

$$= +1.180\ \text{V} - \frac{\left(8.314\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(298.15\ \text{K})}{(1\ \text{mol}\ e^-)\left(96485\ \frac{\text{C}}{\text{mol}\ e^-}\right)}\ln\frac{[1.10][1.00]}{[1.20][0.95]}$$

$$E_{cell} = 1.181\ \text{V}$$

ELECTROCHEMISTRY: PROBLEM 5.3

Sodium metal (Na) can be obtained by electrolyzing molten NaCl. What mass of sodium metal can be produced when molten NaCl is electrolyzed for 10.3 hours with 5.13 A of current?

Half-reaction	$E°$ (V)
Cl_2 (g) + 2 e^- → 2 Cl^- (aq)	+1.358
Na^+ (aq) + e^- → Na (s)	−2.710

— answer —

The reaction we are interested in is the cathodic reaction: Na^+ (aq) + e^- → Na (s).

We can determine the amount of Na using the stoichiometry of the equation above where $n = 1$, $F = 96485 \frac{\text{C}}{\text{mol } e^-}$, and $1\ \text{A} = 1 \frac{\text{C}}{\text{s}}$.

$$m_{\text{Na}} = 10.3\ \text{hr} \times \frac{60\ \text{min}}{1\ \text{hr}} \times \frac{60\ \text{s}}{1\ \text{min}} \times \frac{5.13\ \text{C}}{1\ \text{s}} \times \frac{1\ \text{mol e}^-}{96485\ \text{C}} \times \frac{1\ \text{mol Na}}{1\ \text{mol e}^-} \times \frac{22.99\ \text{g}}{1\ \text{mol Na}} = 45.3\ \text{g Na (s)}$$

NUCLEAR CHEMISTRY: PROBLEM 6.1

For each of the following nuclides, predict the types of radioactive decay and reactants/products of such decays.

– answer –

	Nuclide	Neutron/Proton Ratio	Decay Type	Nuclear Equation
(a)	^{37}Ca	$^{37}_{20}\mathrm{Ca} \rightarrow \frac{17\ \mathrm{n}}{20\ \mathrm{p}}$	electron capture *-or-* position emission	$^{37}_{20}\mathrm{Ca} + {}^{0}_{-1}\beta \rightarrow {}^{37}_{19}\mathrm{K}$ *-or-* $^{37}_{20}\mathrm{Ca} \rightarrow {}^{37}_{19}\mathrm{K} + {}^{0}_{+1}\beta$
(b)	^{34}P	$^{34}_{15}\mathrm{P} \rightarrow \frac{19\ \mathrm{n}}{15\ \mathrm{p}}$	beta decay	$^{34}_{15}\mathrm{P} \rightarrow {}^{34}_{16}\mathrm{S} + {}^{0}_{-1}\beta$
(c)	^{212}Fr	$^{212}_{87}\mathrm{Fr} \rightarrow \frac{125\ \mathrm{n}}{87\ \mathrm{p}}$	alpha decay Z > 83	$^{212}_{87}\mathrm{Fr} \rightarrow {}^{208}_{85}\mathrm{At} + {}^{4}_{2}\alpha$
(d)	^{129}Sb	$^{129}_{51}\mathrm{Sb} \rightarrow \frac{78\ \mathrm{n}}{51\ \mathrm{p}}$	beta decay	$^{129}_{51}\mathrm{Sb} \rightarrow {}^{129}_{52}\mathrm{Te} + {}^{0}_{-1}\beta$

NUCLEAR CHEMISTRY: PROBLEM 6.2

A ^{8}B nuclide decays into a ^{8}Be nuclide through positron emission. Calculate the energy produced from this type of radioactive decay based on the following masses: ^{8}B (8.02460 amu), ^{8}Be (8.00530 amu), and $_{+1}^{0}\beta$ (0.00055 amu).

Recall: 1 amu = 1.6605×10^{-27} kg c = 3.00×10^{8} m/s $1\ \text{J} = 1\ \text{kg} \cdot {}^{\text{m}^2}/_{\text{s}^2}$

– answer –

The reaction we are interested is: $_{5}^{8}\text{B} \rightarrow {}_{4}^{8}\text{Be} + {}_{+1}^{0}\beta$

We can determine the energy released by first finding the mass defect (Δm):

$$\Delta m = \sum m_{\text{products}} + \sum m_{\text{reactans}}$$

$$= [8.00530\ \text{amu} + 0.00055\ \text{amu}] - 8.02460\ \text{amu}$$

$$\Delta m = -0.01875\ \text{amu}$$

Finally, we can use Einstein's equation to convert the mass defect into an energy value:

$$\Delta E = (\Delta m)c^2$$

$$= \left(-0.01875\ \text{amu} \times \frac{1.6605 \times 10^{-27}\ \text{kg}}{1\ \text{amu}}\right)\left(3.00 \times 10^{8}\ \frac{\text{m}}{\text{s}}\right)^2$$

$$\Delta E = -2.80 \times 10^{-12}\ \text{J}$$

NUCLEAR CHEMISTRY: PROBLEM 6.3

A piece of paper from an ancient scroll undergoes ^{14}C-decay with a rate of 9.07 decays/min. A fresh piece of paper also undergoes ^{14}C-decay but with a rate of 13.6 decays/min. If the half-life for ^{14}C-decay is 5730 years, how old is the scroll?

– answer –

The assumption in carbon dating is that the amount of radioactive ^{14}C (N) decreases over time. As such, the older an object is, the lower the ^{14}C-decay rate because radioactive decay follows first-order kinetics:

$$\text{Rate} = kN$$

So, if we compare the ^{14}C-decay rates between the ancient and fresh paper, we can get a ratio of the ^{14}C content:

$$\text{Rate}_t = kN_t = 9.07\frac{\text{decays}}{\text{min}} \qquad \text{Rate}_0 = kN_0 = 13.6\frac{\text{decays}}{\text{min}}$$

$$\frac{\text{Rate}_t}{\text{Rate}_0} = \frac{kN_t}{kN_0} \quad \rightarrow \quad \frac{\text{Rate}_t}{\text{Rate}_0} = \frac{N_t}{N_0} = \frac{9.07}{13.6} = 0.666_9$$

We can now use this ratio in the integrated rate law to find the age of the ancient scroll:

$$t = -\frac{t_{\frac{1}{2}}}{\ln 2}\ln\frac{N_t}{N_0}$$

$$= -\frac{5370\text{ yr}}{\ln 2}\ln 0.666_9$$

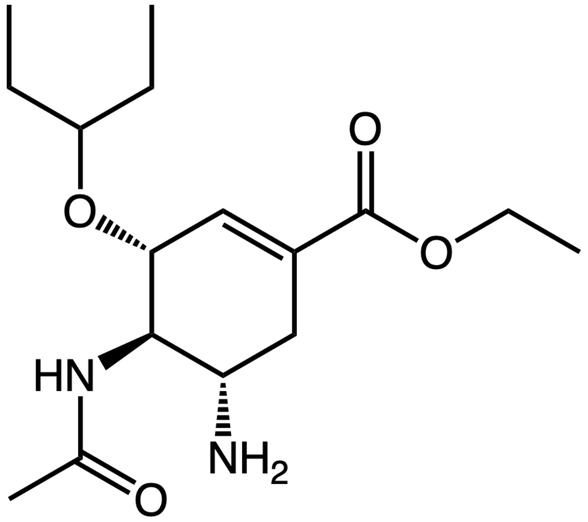
$$t = 3349\text{ yrs old}$$

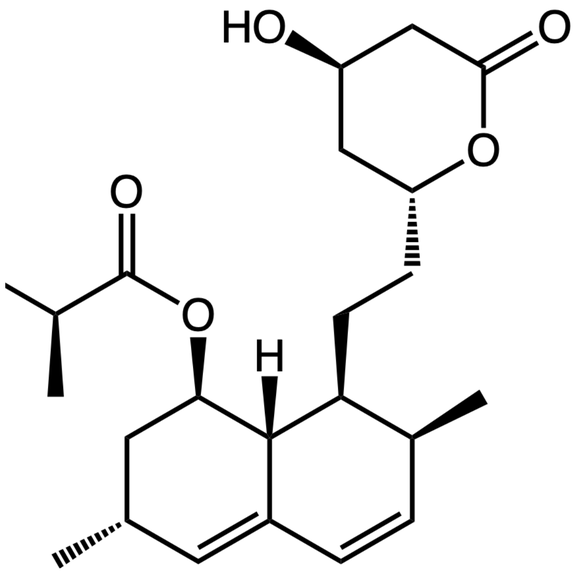
ORGANIC CHEMISTRY: PROBLEM 7.1

For the two compounds shown below, identify if the following functional groups are present.

— answer —

	Functional Group				Functional Group	
(a)	Alcohol	No		(a)	Alcohol	Yes
(b)	Amide	Yes		(b)	Amide	No
(c)	Carboxylic Acid	No		(c)	Carboxylic Acid	No
(d)	Amine	Yes		(d)	Amine	No
(e)	Ester	Yes		(e)	Ester	Yes
(f)	Alkyne	No		(f)	Alkyne	No
(g)	Ether	Yes		(g)	Ether	No
(h)	Alkene	Yes		(h)	Alkene	Yes
(i)	Aldehyde	No		(i)	Aldehyde	No
(j)	Ketone	No		(j)	Ketone	No

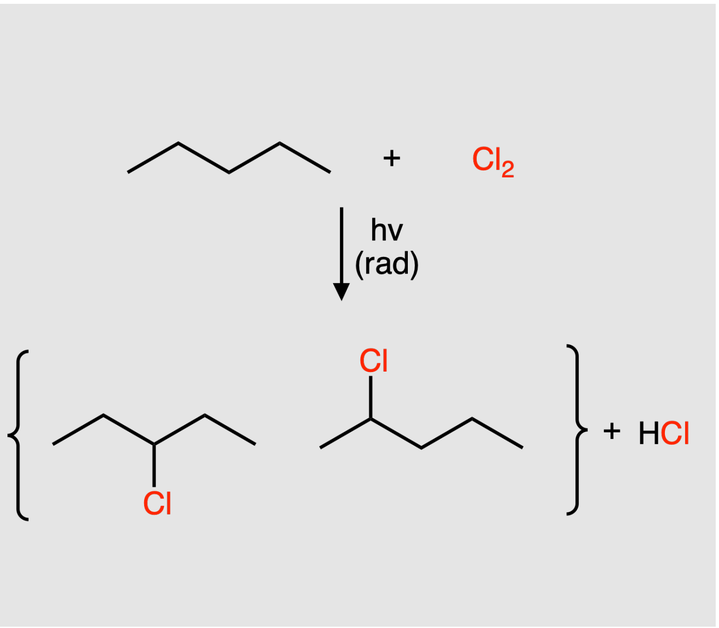


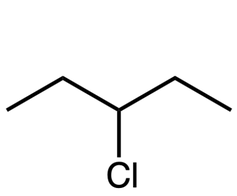


ORGANIC CHEMISTRY: PROBLEM 7.2

Choose the possible product(s) for the reaction between pentane and Cl_2 using UV radiation.

— answer —





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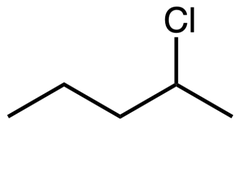

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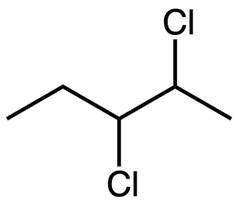

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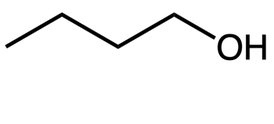

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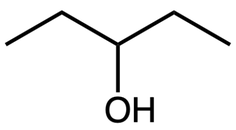

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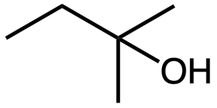

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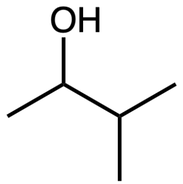

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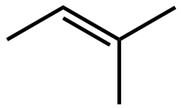

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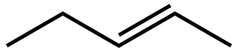

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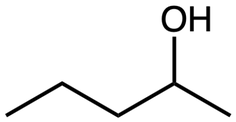

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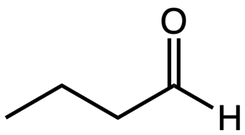

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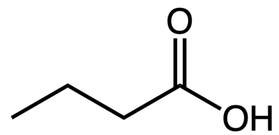

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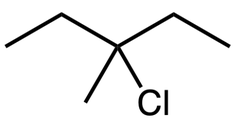

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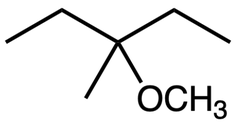

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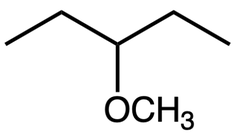

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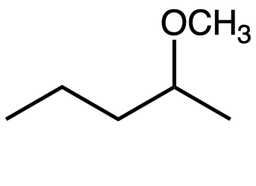

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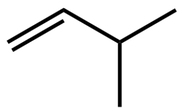

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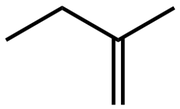

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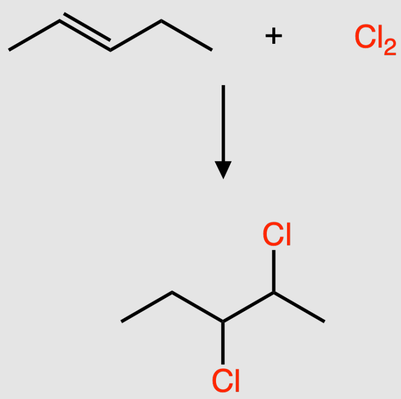
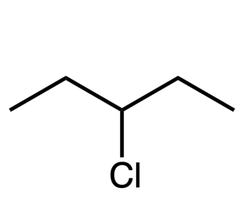
ORGANIC CHEMISTRY: PROBLEM 7.3

Choose the possible product(s) for the addition reaction between 2-pentene and Cl_2.

— answer —





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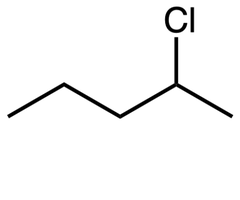

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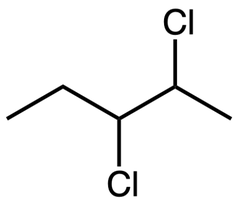

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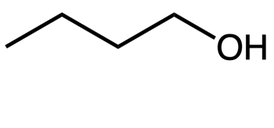

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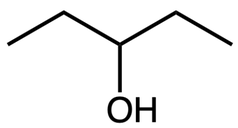

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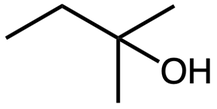

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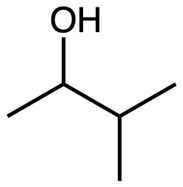

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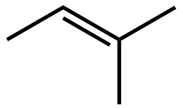

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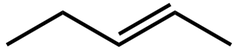

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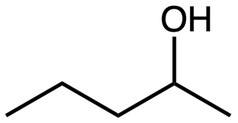

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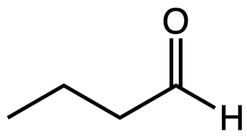

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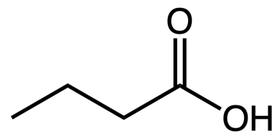

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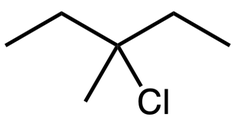

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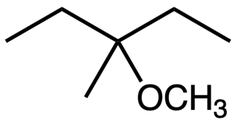

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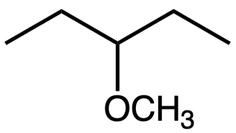

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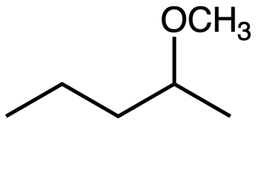

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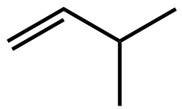

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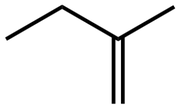

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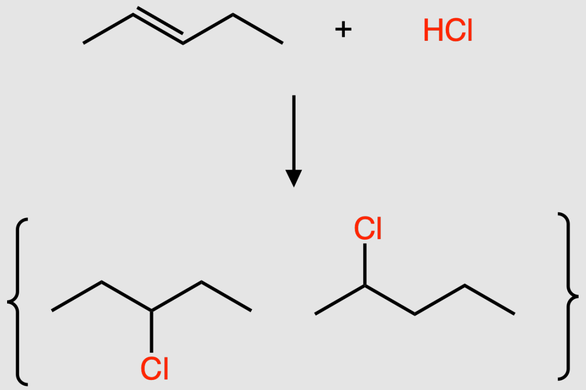
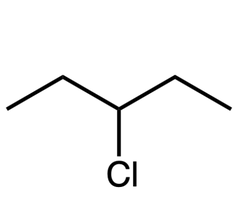
ORGANIC CHEMISTRY: PROBLEM 7.4

Choose the possible product(s) for the addition reaction between 2-pentene and HCl.

— answer —





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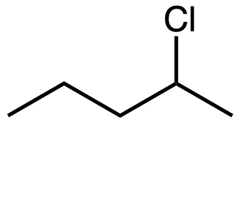

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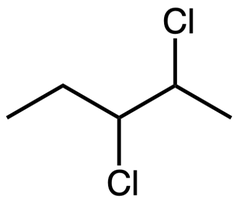

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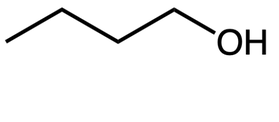

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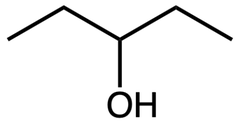

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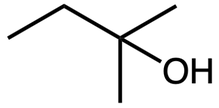

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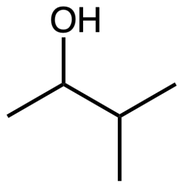

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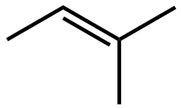

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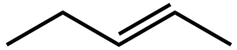

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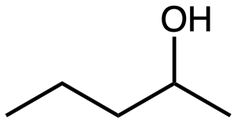

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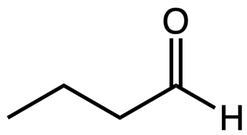

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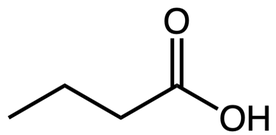

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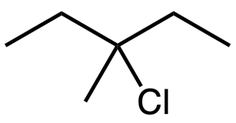

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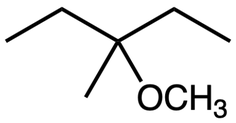

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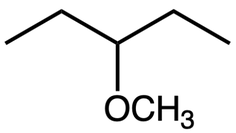

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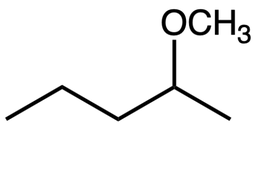

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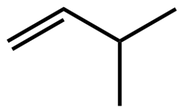

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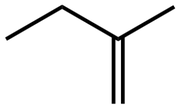

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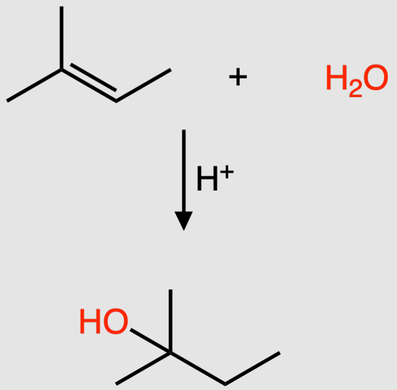
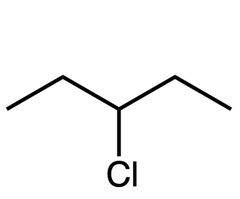
ORGANIC CHEMISTRY: PROBLEM 7.5

Choose the possible major product(s) for the addition reaction between 2-methyl-2-butene, water, and an acid catalyst.

— answer —





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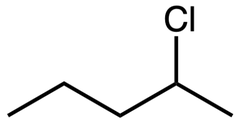

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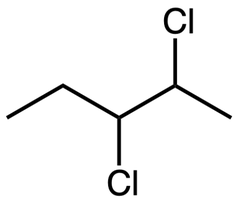

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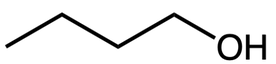

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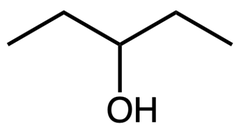

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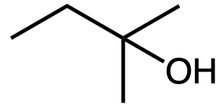

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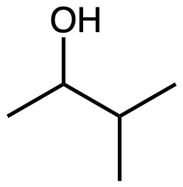

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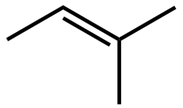

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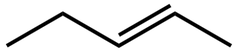

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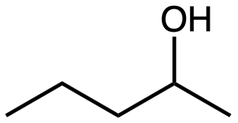

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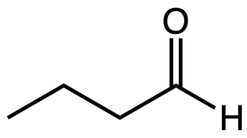

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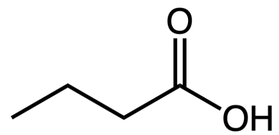

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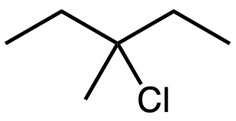

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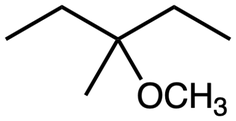

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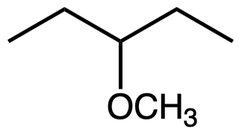

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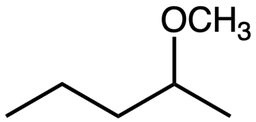

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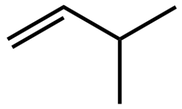

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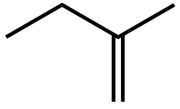


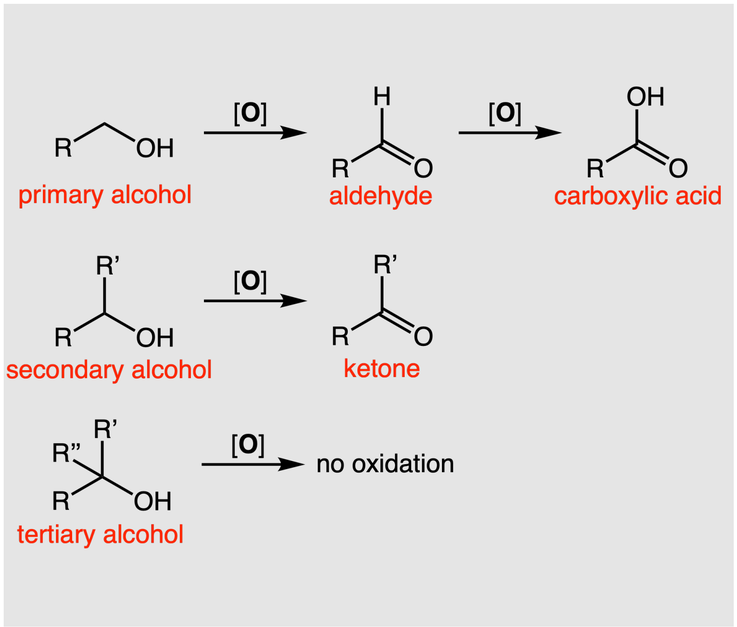
(18)

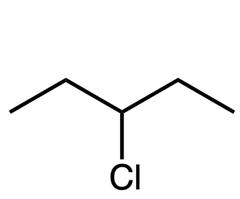
Compound 7 would be the minor compound formed upon addition.

ORGANIC CHEMISTRY: PROBLEM 7.6

Which of the following compounds could be oxidized to produce a ketone?

— answer —

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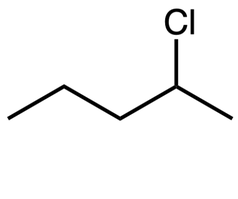

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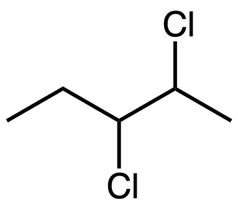

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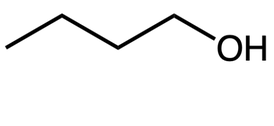

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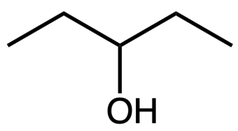

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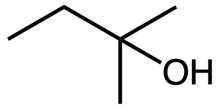

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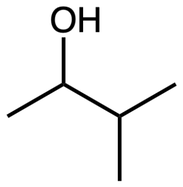

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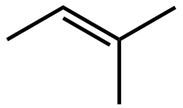
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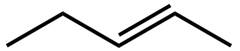
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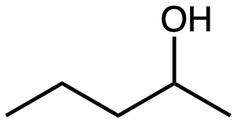

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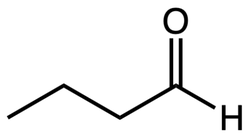

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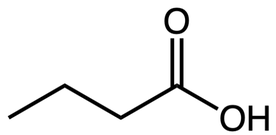

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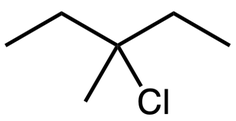

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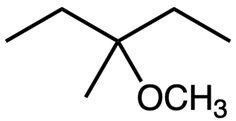

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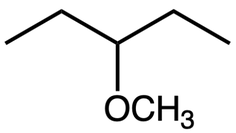

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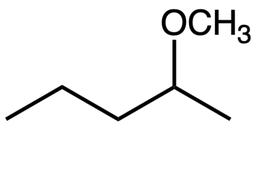

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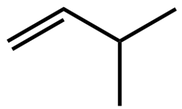
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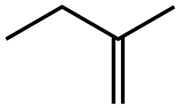
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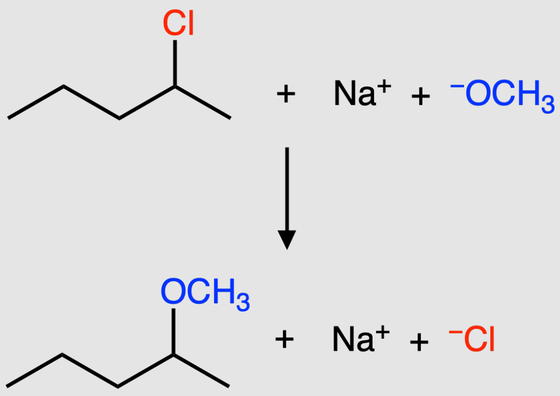
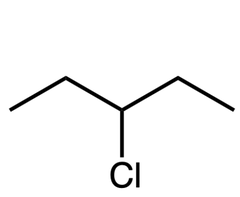
ORGANIC CHEMISTRY: PROBLEM 7.7

Which of the following compound could be mixed with $NaOCH_3$ to make compound **16**?

— answer —





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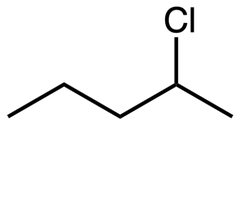

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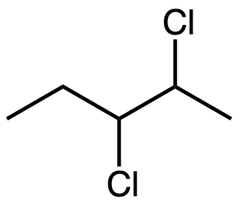

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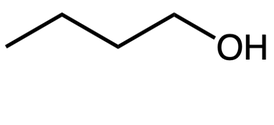

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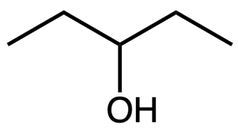

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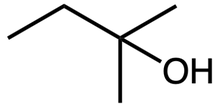

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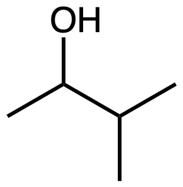

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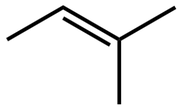

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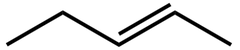

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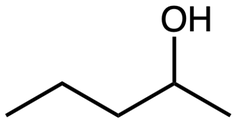

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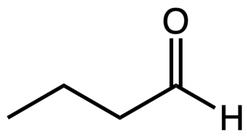

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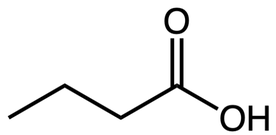

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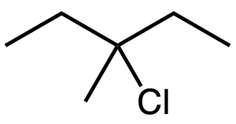

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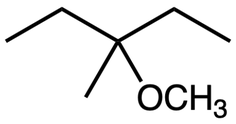

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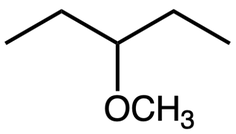

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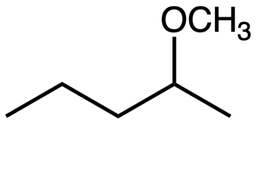

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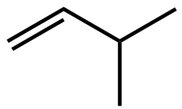

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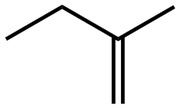

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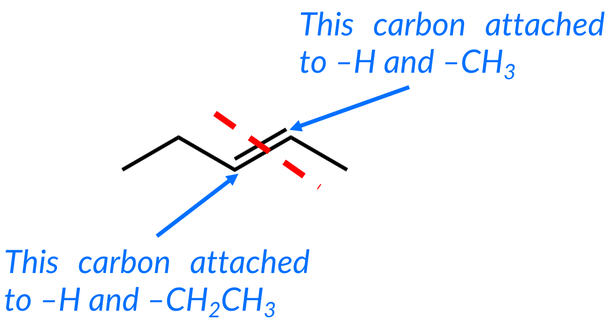
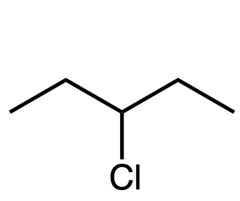
ORGANIC CHEMISTRY: PROBLEM 7.8

Which of the following compounds could exhibit geometric isomerism?

— answer —

In order for a compound to exhibit geometric isomerism (cis/trans or E/Z), you need to look for a structure with an alkene group (8, 9, 17, 18). From the alkenes, you need to look at the groups sticking off of each carbon of the alkene (see red-line). If the groups on each side of the double bond are different from each other (9), the compound can exhibit geometric isomerism.





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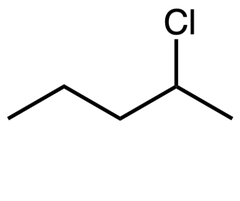

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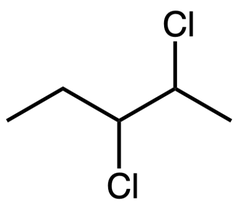

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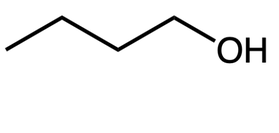

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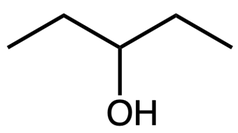

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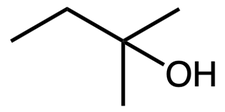

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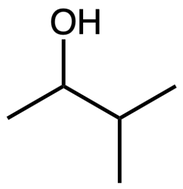

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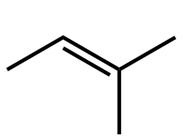

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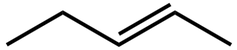

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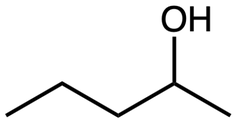

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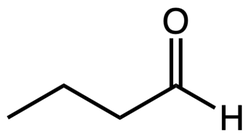

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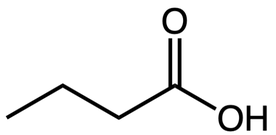

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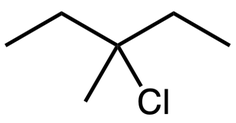

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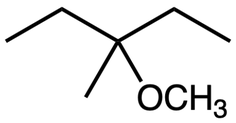

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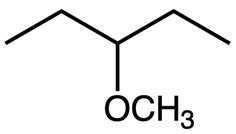

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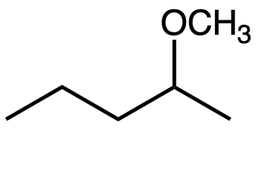

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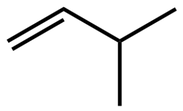

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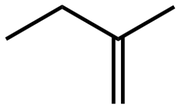

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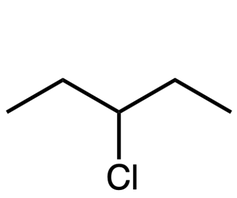
ORGANIC CHEMISTRY: PROBLEM 7.8

Which of the following compounds contains a chiral carbon center?

— answer —

A chiral carbon center is an sp^3-hybridized carbon attached to 4 different groups.

Chiral centers have been identified with red dots.



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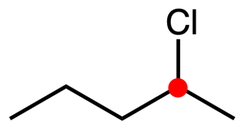

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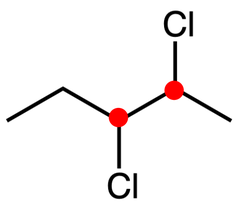

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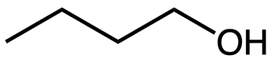

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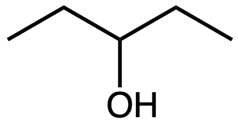

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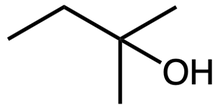

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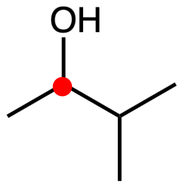

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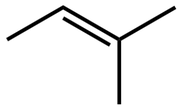

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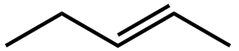

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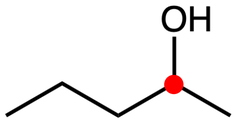

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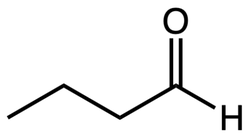

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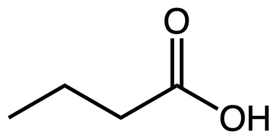

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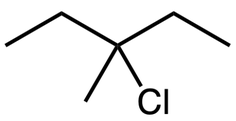

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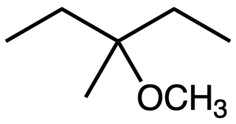

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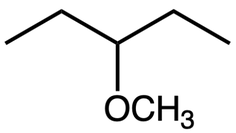

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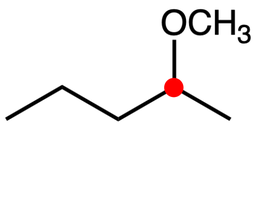

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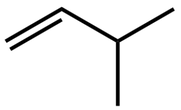

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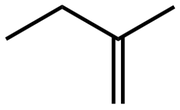

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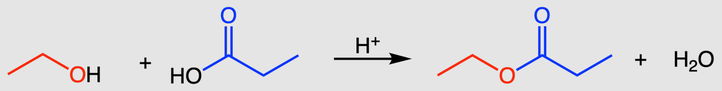
ORGANIC CHEMISTRY: PROBLEM 7.9

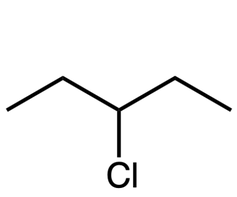
Choose any two compounds that can be mixed together with an acid catalyst to produce an ester via condensation.

— answer —

An ester can only be formed from the acid-catalyzed condensation reaction between a carboxylic acid (12) and alcohols (4-6, 7, 10, 12).

For instance,

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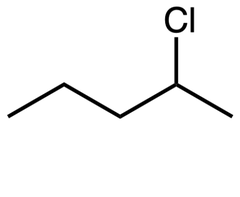
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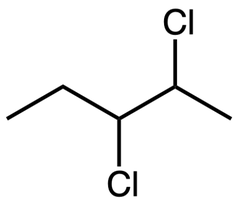
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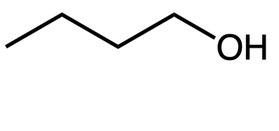
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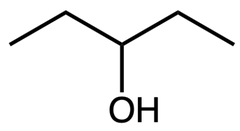
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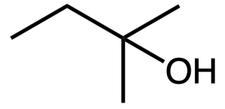
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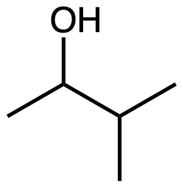
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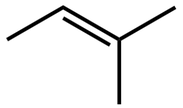
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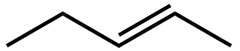
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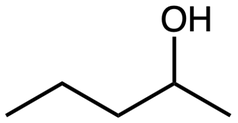
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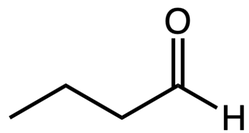
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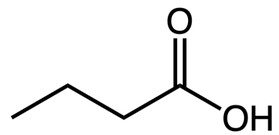
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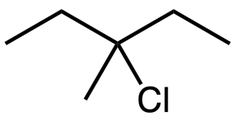
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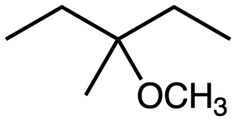
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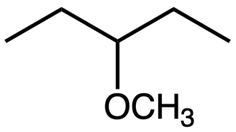
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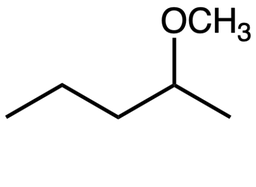
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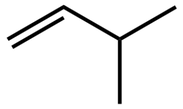
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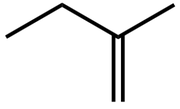
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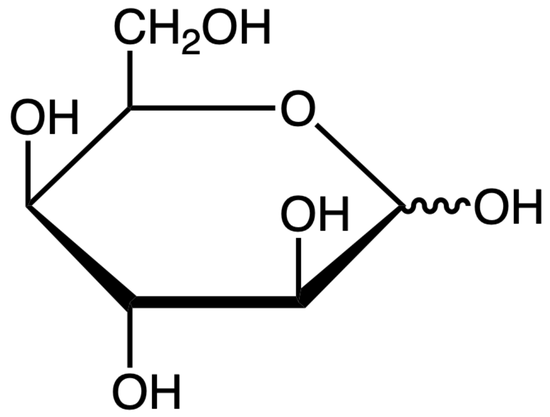
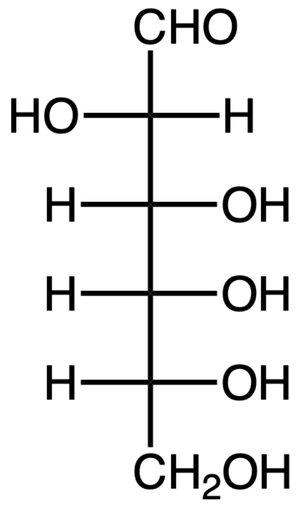
BIOCHEMISTRY: PROBLEM 8.1

The Haworth projection for the D-Idose pyranose is shown below. Which is the correct Fischer projection for D-Idose?

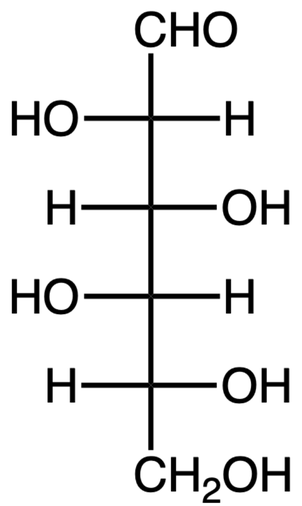
— answer —



D-Idose



(A)



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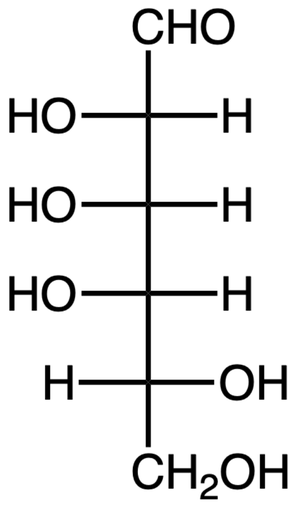


(C)

Recall:

- We number sugars from the top-to-bottom in the Fischer projection.
- The anomeric carbon is the last (bottom-most) chiral center in the Fischer projection.
- The anomeric carbon bonds to the C=O at the top of the sugar in the Fischer projection.
- For the orientation of the –OH groups:

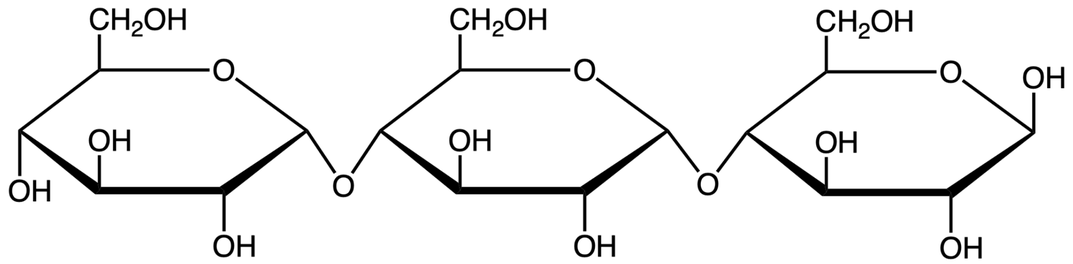
  –OH groups that are on the right side of a Fischer projection stick down in the Haworth projection.

  –OH groups that are on the left side of a Fischer projection stick up in the Haworth projection.

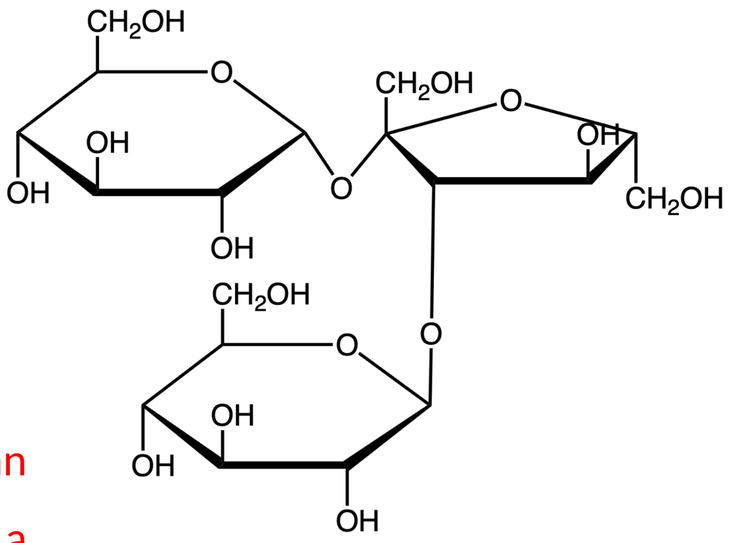
BIOCHEMISTRY: PROBLEM 8.2

The trisaccharaides maltotriose, melezitose, and kestose are shown below. Which is a reducing sugar?

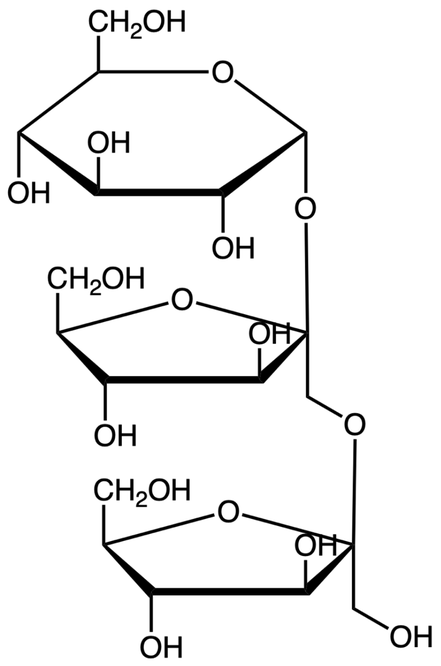
— answer —



Maltotriose



Melezitose



Kestose

Reducing sugars have anomeric carbons that are attached to an O atom and an –OH group. This O-C-OH linkage is called a hemiacetal functional group.

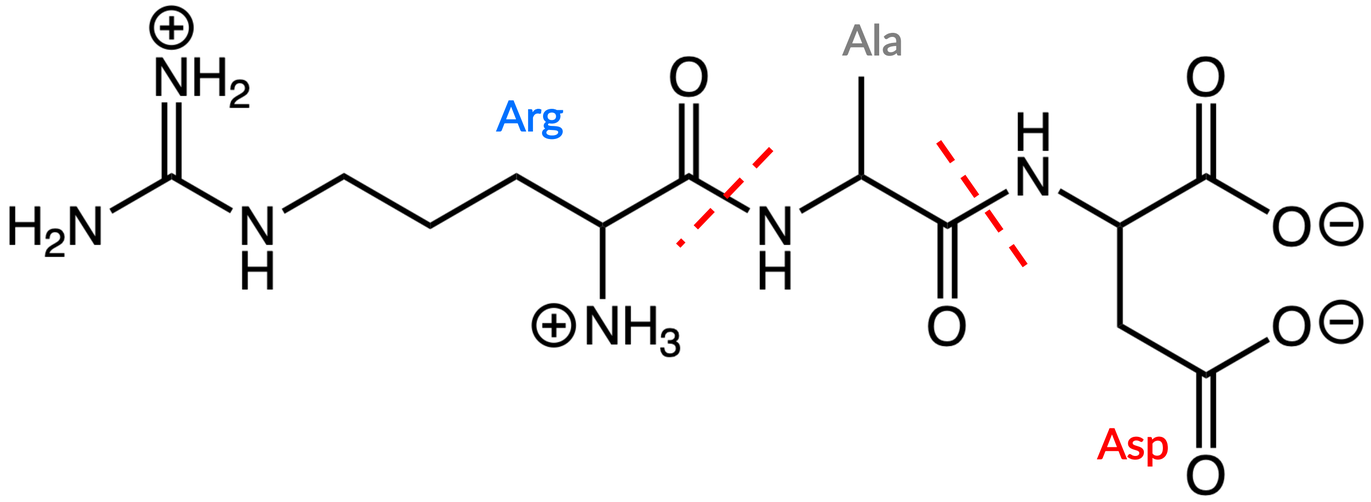
Only maltotriose satisfies this criterion.

Melezitose and kestose have O-C-CH_2OH linkages.

BIOCHEMISTRY: PROBLEM 8.3

The tripeptide shown below is comprised of three amino acids. Which amino acid would travel the farthest toward the positive electrode during electrophoresis with a pH = 6 buffer.

— answer —



Aspartic acid (pI = 2.8) will travel the farthest toward the positive electrode because it is negatively charged in pH = 7 solution.

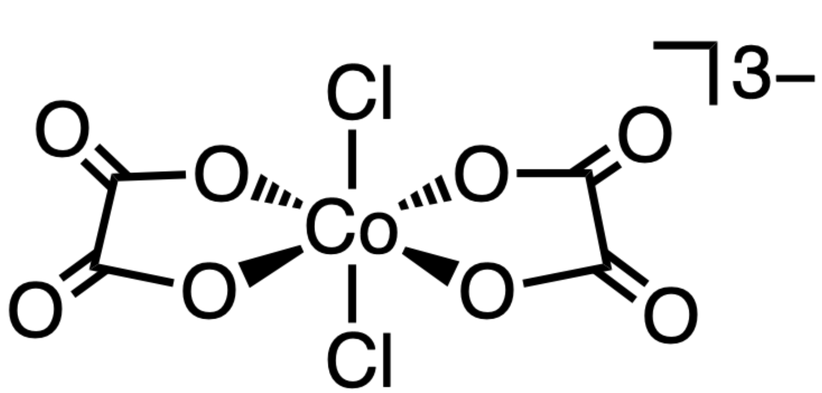
Alanine (pI = 6.0) will not travel to either electrode because it is neutral at pH = 7 solution.

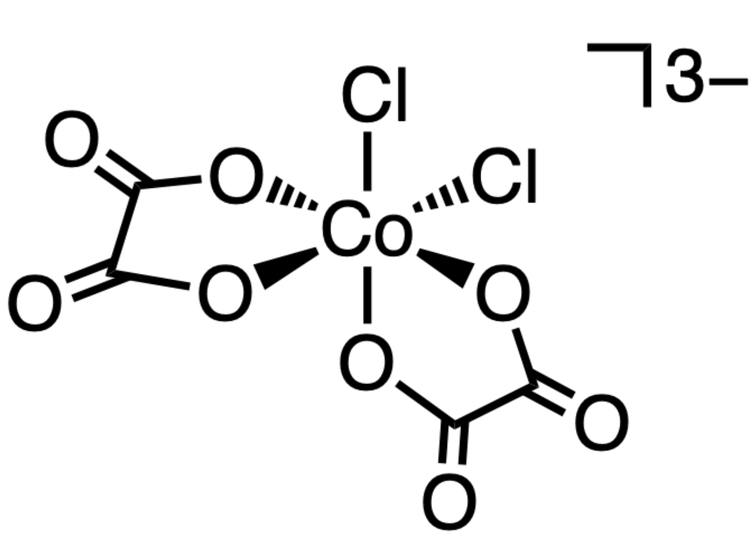
Arginine (pI = 10.8) will travel the farthest toward the negative electrode because it is positively charged in pH = 7 solution.

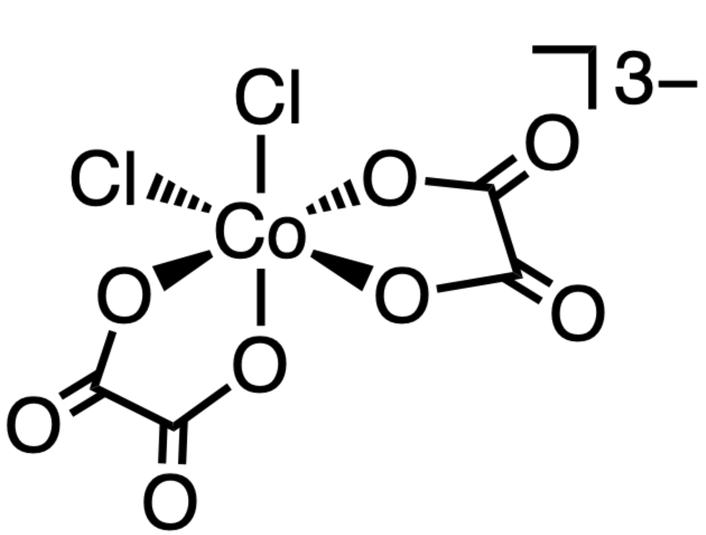
TRANSITION METALS: PROBLEM 9.1

Dichlorobisoxalatocobaltate(III) can exist as three optical isomer. One is drawn below. Draw the other two stereoisomers.

— answer —







These two are enantiomers (non-superimposable mirror images).

TRANSITION METALS: PROBLEM 9.2

You have three colored solutions: (1) violet, (2) yellow, and (3) green. Match each of the colored solutions (1–3) to the corresponding complex ions: (a) $[Cr(NH_3)_6]^{3+}$, (b) $[Cr(H_2O)_6]^{3+}$, and (c) $[Cr(H_2O)_4Cl_2]^{+}$.

Spectrochemical series: $CN^- > NO_2^- > CN^- > en > NH_3 > H_2O > F^- > Cl^- > Br^- > I^-$

— answer —

Recall that the complementary color of the observed color of a complex is an indirect estimate of the energy splitting (Δ_o). As light passes through the solution, photons of a specific wavelength equal to the value of Δ_o are absorbed by the complex, while all other wavelengths of light are transmitted through the solution for our eyes to observe.

Therefore, we need to consider the complimentary colors for each solution:

Solution	Observed Color	Absorbed Color (~Δ_o)	Complex	Reasoning
(1)	Violet (λ_{obs} ~410 nm)	Yellow (λ_{abs} ~570 nm)	$[Cr(H_2O)_6]^{3+}$	H_2O is a low-field ligand, so Δ_o is relatively small and λ_{abs} is large.
(2)	Yellow (λ_{obs} ~570 nm)	Blue (λ_{abs} ~450 nm)	$[Cr(NH_3)_6]^{3+}$	NH_3 is a high-field ligand, so Δ_o is relatively large and λ_{abs} is small.
(3)	Green (λ_{obs} ~520 nm)	Red (λ_{abs} ~650 nm)	$[Cr(H_2O)_4Cl_2]^{+}$	H_2O and Cl^- are low-field ligands, so Δ_o is relatively small and λ_{abs} is large. Cl^- is a stronger low-field ligand than H_2O, so Δ_o is even smaller than $[Cr(H_2O)_6]^{3+}$.

TRANSITION METALS: PROBLEM 9.3

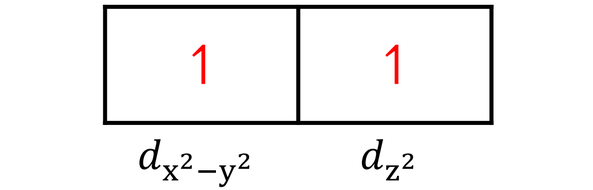
For each pair of complex ions, determine: (a) the number of 3*d* electrons and oxidation state, (b) if each is high- or low-spin, (c) if each is paramagnetic or diamagnetic, and (d) the magnetic moment (μ_{eff}).

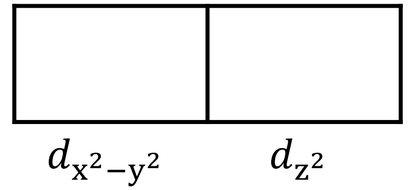
Spectrochemical series: $CN^- > NO_2^- > CN^- > en > NH_3 > H_2O > F^- > Cl^- > Br^- > I^-$

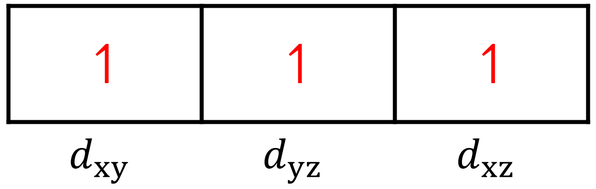
— answer —

First, determine the number of d electrons for each set of complex ions. Then, use the spectrochemical series to determine whether the complex is high- or low-spin and fill the crystal field diagram appropriately. Lastly,

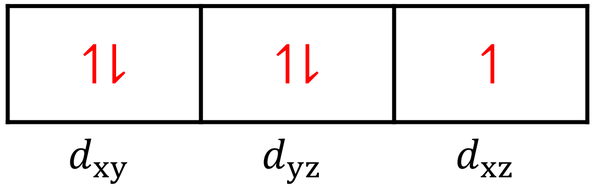
$$\mu_{eff} = \sqrt{n(n+2)} \qquad ; n = \#\ \text{unpaired}\ e^-$$







Fe^{3+} high-spin



Fe^{3+}: low-spin

	Complex ions	No. 3d electrons?	Spin?	Magnetism?	μ_{eff} (B.M.)
(i)	$[Fe(H_2O)_6]Cl_3$	Fe^{3+}: [Ar] $3d^5$	High-spin	Paramagnetic	$\mu_{eff} = \sqrt{5(5+2)} = 5.92$
	$Na_3[Fe(CN)_6]$		Low-spin	Paramagnetic	$\mu_{eff} = \sqrt{1(1+2)} = 1.73$
(ii)	$[Co(NH_3)_6]Cl_3$	Co^{3+}: [Ar] $3d^6$	Low-spin	Diamagnetic	$\mu_{eff} = \sqrt{0(0+2)} = 0$
	$K_3[CoF_6]$		High-spin	Paramagnetic	$\mu_{eff} = \sqrt{4(4+2)} = 4.90$