There are 30 Questions in this set.

1. The diagram below is a representation of the crystal lattice structure of a certain compound. If the gray spheres are represented by $A$ and orange spheres $B$, what is the formula of this compound?

a. AB
b. $\mathrm{A}_{14} \mathrm{~B}_{8}$
c. $\mathrm{AB}_{2}$
d. $A_{2} B$
e. $A_{7} B_{4}$
2. Experimentally, the lattice energy of a crystalline compound is determined using a Born-Haber cycle and applying Hess' law. Determine the lattice energy ( $\mathrm{kJmol}^{-1}$ ) for NaCl given that:

| Enthalpy of formation of $\mathrm{NaCl}(\mathrm{s})$ | $-411 \mathrm{~kJ} / \mathrm{mol}$ |
| :--- | :--- |
| Enthalpy of sublimation of $\mathrm{Na}(\mathrm{s})$ | $+109 \mathrm{~kJ} / \mathrm{mol}$ |
| Ionization energy of $\mathrm{Na}(\mathrm{g})$ | $+495 \mathrm{~kJ} / \mathrm{mol}$ |
| Enthalpy of dissociation of $\mathrm{Cl}_{2}(\mathrm{~g})$ | $+244 \mathrm{~kJ} / \mathrm{mol}$ |
| Electron affinity of the $\mathrm{Cl}(\mathrm{g})$ | $-349 \mathrm{~kJ} / \mathrm{mol}$ |

f. $788 \mathrm{~kJ} / \mathrm{mol}$
g. $910 \mathrm{~kJ} / \mathrm{mol}$
h. $\quad-34 \mathrm{~kJ} / \mathrm{mol}$
i. $\quad 88 \mathrm{~kJ} / \mathrm{mol}$
j. $\quad 644 \mathrm{~kJ} / \mathrm{mol}$
3. It is well-known that water can form multiple different solid forms at high pressures and/or low temperatures. One such form is ice Ic which is a metastable crystalline variant of ice. It has a face-centered cubic (FCC) unit cell and 4 more molecules additionally fill all its tetrahedral holes. The cell edge length (a) is 0.636 nm . Calculate the density of ice Ic.
a. $0.93 \mathrm{~g} / \mathrm{cm}^{3}$
b. $\quad 1.35 \mathrm{~g} / \mathrm{cm}^{3}$
c. $\quad 0.12 \mathrm{~g} / \mathrm{cm}^{3}$
d. $2.09 \mathrm{~g} / \mathrm{cm}^{3}$
e. $1.03 \mathrm{~g} / \mathrm{cm}^{3}$
4. How many isomeric forms of dichlorocyclobutane can exist? How many of them are optically active?
a. 5, of which none is optically active
b. 6, of which 2 are optically active
c. 7, of which 4 are optically active
d. 8 , of which 6 are optically active
e. 9 , of which 6 are optically active
5. Names of organic molecules can sometimes be very lengthy and difficult to understand. The molecule below is called (1A)-1-((B)-2-(tert-butyl)-3-(1-iodoethylidene)cyclopropyl)ethan-1-ol ,where letters A and $\mathbf{B}$ are used instead of proper stereodescriptors. What are the correct stereodescriptors for the molecule?

a. $\mathrm{A}=\mathrm{R}, \mathrm{B}=\mathrm{Z}$
b. $A=S, B=E$
c. $A=Z, B=S$
d. $\mathrm{A}=R, \mathrm{~B}=\mathrm{E}$
e. $\mathrm{A}=\mathrm{Z}, \mathrm{B}=R$
6. Which of the following is NOT present in the molecule from question \#5?
a. sp-hybridized atom
b. asymmetric center
c. m-bond
d. quaternary carbon
e. heteroatom
7. Which position is the most reactive towards electrophilic aromatic substitution in the following molecule?

a. 1
b. 2
c. 3
d. 4
e. 5

For questions 8-11, consider the following synthetic scheme:


Which starting compound A was most likely used in this synthesis?
a.

b.

c.

d.

e.

9. Which compound or set of compounds can be used in step B of this synthesis?
a.

b. $\mathrm{NC}=\mathrm{CN}$
c. $(\mathrm{CN})_{2}$
d.
$\mathrm{C}_{2} \mathrm{H}_{2}, \mathrm{KCN}$

e.
10. What is the final product $(\mathrm{C})$ in this pathway?
a.

b.

c.

d.

e.

11. Which of the following compounds is active in Raman but not in IR spectroscopy?
a. $\mathrm{H}_{2}$
b. CO
c. $\mathrm{H}_{2} \mathrm{O}$
d. $\mathrm{CO}_{2}$
e. $\mathrm{CH}_{4}$
12. Absorption of the compound $A(0.010 \mathrm{M})$ and compound $B(0.020 \mathrm{M})$ solutions was measured spectrophotometrically in 0.50 cm cuvettes. They were found to be equal to 1.532 and 0.246 at 538 nm and 0.122 and 1.347 at 645 nm respectively. Calculate the concentrations of $A$ and $B$ in an unknown solution if it is absorbance is 1.034 at 538 nm and 1.678 at 645 nm .
a. $C(A)=1.2 \mathrm{mM}, C(B)=12 \mathrm{mM}$
b. $C(A)=2.4 \mathrm{mM}, C(B)=12 \mathrm{mM}$
c. $C(A)=1.2 \mathrm{mM}, \mathrm{C}(B)=6.0 \mathrm{mM}$
d. $C(A)=3.4 \mathrm{mM}, C(B)=6.0 \mathrm{mM}$
e. $C(A)=3.4 \mathrm{mM}, C(B)=12 \mathrm{mM}$
13. Calculate the molar solubility (in $\mathrm{mol} \mathrm{L}^{-1}$ ) of a divalent metal sulfide in water at $25^{\circ} \mathrm{C}$ and $\mathrm{pH}=3$ if its solubility product is equal to $8.0 \times 10^{-27}$ (for $\mathrm{H}_{2} \mathrm{~S} \mathrm{Ka}_{1}=9.1 \times 10^{-8}, \mathrm{Ka}_{2}=1.0 \times 10^{-18}$ ).
a. $s=3.0 \times 10^{-4} \mathrm{M}$
b. $s=8.0 \times 10^{-6} \mathrm{M}$
c. $s=8.0 \times 10^{-10} \mathrm{M}$
d. $s=9.4 \times 10^{-10} \mathrm{M}$
e. $s=8.9 \times 10^{-14} \mathrm{M}$

## Consider the following analysis of the alloy for questions 14-17.

The alloy contains cadmium, tin, bismuth, and lead. A sample of the alloy weighing 1.2860 g was treated with concentrated $\mathrm{HNO}_{3}$. The precipitated compound containing metal A was isolated, thoroughly washed, dried, and calcinated. The mass of the residue after calcination was $\mathbf{0 . 3 2 6 5} \mathbf{g}$.

Excess aqueous ammonia was added to the solution obtained after separating the precipitate. Metal compound $B$ remained in the solution, and the remaining metals were precipitated in the form of poorly soluble compounds. After separating the precipitate, hydrogen sulfide was bubbled through the solution (until saturation). The precipitate containing metal B was separated, washed, and dried, its mass was 0.6613 g .

The precipitate containing compounds of metals $\mathbf{C}$ and D was treated with an excess of NaOH solution. The solution containing metal $\mathbf{C}$ and precipitate were quantitatively separated.

The alkaline solution was acidified with nitric acid to $\mathrm{pH} 5-6$, after which an excess of potassium chromate was added to the clear solution. The obtained yellow precipitate was separated, washed, and transferred quantitatively into a laboratory beaker, to which crystalline potassium iodide and diluted $\mathrm{H}_{2} \mathrm{SO}_{4}$ were added subsequently. The formed iodine was titrated with a solution of sodium thiosulfate (with starch as an indicator). 18.46 mL of 0.1512 N sodium thiosulfate solution was used for titration.

The last metal D , which was present in the form of its poorly soluble compound, was converted into an even less soluble phosphate. The mass of this phosphate was 0.4675 g .
14. Identify metal A and find its mass fraction in the alloy.
a. $\mathrm{Pb}(25 \%)$
b. $\mathrm{Pb}(20 \%)$
c. $\mathrm{Sn}(20 \%)$
d. $\mathrm{Sn}(25 \%)$
e. $\mathrm{Bi}(25 \%)$
15. Identify metal B and find its mass fraction in the alloy.
a. $\mathrm{Cd}(20 \%)$
b. $\mathrm{Cd}(40 \%)$
c. $\mathrm{Bi}(20 \%)$
d. $\mathrm{Bi}(40 \%)$
e. $\mathrm{Pb}(20 \%)$
16. Calculate the amount of chromate anions in the yellow precipitate using the data from the back titration experiment.
a. 0.47 mmol
b. 0.93 mmol
c. $\quad 1.40 \mathrm{mmol}$
d. $\quad 2.79 \mathrm{mmol}$
e. 8.37 mmol
17. Identify metal C and find its mass fraction in the alloy.
a. $\mathrm{Bi}(20 \%)$
b. $\mathrm{Pb}(15 \%)$
c. $\quad \mathrm{Cd}(15 \%)$
d. Sn (15 \%)
e. $\mathrm{Sn}(20 \%)$
18. You are an employee of the resource center of the Department of Chemistry and you have received a request to determine the structure of an unknown substance. With the help of HRMS, its formula $\mathrm{C}_{4} \mathrm{H}_{6} \mathrm{O}_{2}$ was established. Choose the correct substance based on the ${ }^{1} \mathrm{H}$ spectrum below.

a.

b.

c.

d.

e. COOMe
19. From the list below, choose the entry with only 18-e complexes.
a. $\mathrm{Fe}(\mathrm{CO})_{5},\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right] \mathrm{Cl}_{2}$
b. $\quad \mathrm{V}(\mathrm{CO})_{6},\left[\mathrm{Zn}\left(\mathrm{NH}_{3}\right)\right]_{4} \mathrm{Cl}_{2}$
c. $\mathrm{Na}_{2}\left[\mathrm{TiF}_{6}\right], \mathrm{K}_{3}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$
d. $\mathrm{K}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right], \mathrm{Na}_{2}\left[\mathrm{PtCl}_{4}\right]$
e. $\mathrm{Mn}_{2}(\mathrm{CO})_{10},\left[\mathrm{Zn}\left(\mathrm{NH}_{3}\right)_{4}\right] \mathrm{Cl}_{2}$

Metal X, dissolved in an excess of dilute hydrochloric acid, forms a blue solution, which turns dark green when exposed to air. Upon treatment with an aqueous alkali solution, a green precipitate first forms, but it dissolves in excess alkali to form a bright green solution. This solution becomes yellow if mixed with chlorine water, and upon subsequent acidification, it turns orange-red. The final solution can be used as a strong oxidizer.

Name the metal $\mathbf{X}$.
a. Fe
c. Cr
b. Mn
d. Ti
e. V
21. Conversion of benzoyl peroxide to diethyl ether (1st order reaction) at 320 K in 10 minutes achieved $67.2 \%$ completion. Calculate the half-conversion time for the reaction.
a. $\quad \mathrm{T}_{1 / 2}=3.11 \mathrm{~min}$
b. $\mathrm{T}_{1 / 2}=4.32 \mathrm{~min}$
c. $\quad \mathrm{T}_{1 / 2}=6.22 \mathrm{~min}$
d. $\mathrm{T}_{1 / 2}=6.72 \mathrm{~min}$
e. $\mathrm{T}_{1 / 2}=17.4 \mathrm{~min}$
22. Two parallel reactions occur in the system:

$$
\begin{aligned}
& A+B \rightarrow \text { products }\left(k_{1}\right), \\
& A+C \rightarrow \text { products }\left(k_{2}\right)
\end{aligned}
$$

The ratio $k_{1} / k_{2}=7$. The initial concentrations of substances $B$ and $C$ are the same. By a certain time, $50 \%$ of substance $B$ has reacted. What part of substance $C$ has reacted by this moment?
a. $0.8 \%$
b. $3.5 \%$
c. $7.1 \%$
d. $14 \%$
e. $43 \%$
23. A steady-state approximation is a useful method for determining the rate law of a process. In it, concentrations of all transient intermediates are assumed to be constant, and, thus, their rate of formation is equal to their rate of consumption.

The conversion reaction of para-hydrogen to ortho-hydrogen (spin isomers of hydrogen) proceeds according to the following mechanism (where M is an inert particle):

$$
\begin{gathered}
p-\mathrm{H}_{2}+\mathrm{M}=\mathrm{H}+\mathrm{H}+\mathrm{M}\left(\mathrm{k}_{1}\right) \\
\mathrm{H}+\mathrm{p}-\mathrm{H}_{2}=\mathrm{H}+o-\mathrm{H}_{2}\left(\mathrm{k}_{2}\right) \\
\mathrm{H}+\mathrm{H}+\mathrm{M}=p-\mathrm{H}_{2}+\mathrm{M}\left(\mathrm{k}_{3}\right)
\end{gathered}
$$

Using the steady-state approximation, find the rate law for the formation of $o-\mathrm{H}_{2}$.
a. $\quad r=\frac{k_{1} k_{2}}{k_{3}}\left[p-H_{2}\right]^{2}$
b. $r=\frac{k_{1} k_{2}}{k_{3}}\left[p-H_{2}\right]^{3 / 2}$
c. $\quad r=\sqrt{k_{1}} k_{2}\left[p-H_{2}\right]^{3 / 2}$
d. $\quad r=k_{1} k_{2}\left[p-H_{2}\right]$
e. $r=k_{2} \sqrt{\frac{k_{1}}{k_{3}}}\left[p-H_{2}\right]^{3 / 2}$

The decomposition of dimethyl ether:

$$
\mathrm{CH}_{3} \mathrm{OCH}_{3}(\mathrm{~g}) \rightarrow \mathrm{CH}_{4}(\mathrm{~g})+\mathrm{CO}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g})
$$

quite satisfactorily follows the 1 st order reaction equation.

Using the data below, calculate the rate constant for this reaction.

| Time (sec) | 0 | 219 | 299 | 564 | $\infty$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| P, mmHg | 420 | 954 | 1054 | 1198 | 1258 |

a. $\mathrm{k}=9.3 \times 10^{-4} \mathrm{c}^{-1}$
b. $\mathrm{k}=3.7 \times 10^{-3} \mathrm{c}^{-1}$
c. $\mathrm{k}=4.7 \times 10^{-3} \mathrm{c}^{-1}$
d. $\mathrm{k}=6.0 \times 10^{-3} \mathrm{c}^{-1}$
e. $k=1.3 c^{-1}$

## The questions 25-27 below are intended to be solved together.

Polymers are organic and inorganic molecules with a large molecular weight, consisting of a large number of repeating structural fragments called monomers. For example, when polymerizing ethylene $\mathrm{C}_{2} \mathrm{H}_{4}$, a long chain consisting of $\mathrm{CH}_{2}$ groups is formed:

$$
\mathrm{nCH}_{2}=\mathrm{CH}_{2} \rightarrow\left(-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\right)_{\mathrm{n}}
$$

The number n is called the degree of polymerization.
25. The thermal effect of this reaction can be assessed, for example, from the tabulated values of binding energies: $\mathrm{E}(\mathrm{C}-\mathrm{C})=332 \mathrm{~kJ} / \mathrm{mol} ; \mathrm{E}(\mathrm{C}=\mathrm{C})=588 \mathrm{~kJ} / \mathrm{mol}$. Estimate the enthalpy of this reaction using the values of binding energies (per 1 mole of $\mathrm{C}_{2} \mathrm{H}_{4}$ ).
a. $-45.0 \mathrm{~kJ} / \mathrm{mol}$
b. $-76.0 \mathrm{~kJ} / \mathrm{mol}$
c. $-136 \mathrm{~kJ} / \mathrm{mol}$
d. $-256 \mathrm{~kJ} / \mathrm{mol}$
e. $-844 \mathrm{~kJ} / \mathrm{mol}$
26. It is possible to use another approach: to compare polyethylene with low-molecular analogues alkanes, also consisting of series-connected $\mathrm{CH}_{2}$ groups. The standard enthalpies of formation of gaseous alkanes $\mathrm{C}_{2} \mathrm{H}_{6}, \mathrm{C}_{3} \mathrm{H}_{8}$ and $\mathrm{C}_{4} \mathrm{H}_{10}$ are $-84.0,-105.0$ and $-126.0 \mathrm{~kJ} / \mathrm{mol}$, respectively, and the enthalpy of formation of ethylene is $52.4 \mathrm{~kJ} / \mathrm{mol}$. Estimate the enthalpy of polymerization reaction (per 1 mole of $\mathrm{C}_{2} \mathrm{H}_{4}$ ).
a. $\quad-56.4 \mathrm{~kJ} / \mathrm{mol}$
b. $-94.4 \mathrm{~kJ} / \mathrm{mol}$
c. $-135 \mathrm{~kJ} / \mathrm{mol}$
d. $-247 \mathrm{~kJ} / \mathrm{mol}$
e. $-756 \mathrm{~kJ} / \mathrm{mol}$
27. The enthalpy of the polymerization reaction can also be determined from experimental data. When 1 g of polyethylene was burned in a calorimeter bomb, 46.50 kJ of heat was released (recalculated for $\mathrm{T}=$ 298 K ). The standard enthalpies of formation of carbon dioxide and liquid water are -393.5 and -285.8 $\mathrm{kJ} / \mathrm{mol}$, respectively. Based on these data, determine the enthalpy of polymerization.
a. $-75.4 \mathrm{~kJ} / \mathrm{mol}$
b. $-80.3 \mathrm{~kJ} / \mathrm{mol}$
c. $-109 \mathrm{~kJ} / \mathrm{mol}$
d. $-156 \mathrm{~kJ} / \mathrm{mol}$
e. $-633 \mathrm{~kJ} / \mathrm{mol}$

## Use the following information for questions 28 and 29.

A Latimer diagram of a chemical element is a summary of the standard electrode potential data of that element. In a Latimer diagram, the most highly oxidized form of the element is on the left side, with successively lower oxidation states on the right side. The species are connected by arrows, and the numerical value of the standard potential (in volts) for the reduction is written at each arrow.

(5)
28. For the Latimer diagram above, calculate $\mathrm{E}_{\mathrm{x}}{ }^{\text {. }}$
a. -0.254 V
b. 0.254 V
c. -0.876 V
d. -0.976 V
e. 0.976 V
29. Determine $\Delta \mathrm{G}^{\circ}$ for the reaction of disproportionation of $\mathrm{VO}^{2+}$ (per 1 mole of $\mathrm{VO}_{2}{ }^{+}$).
a. $\quad-63.97 \mathrm{~kJ} / \mathrm{mol}$
b. $63.97 \mathrm{~kJ} / \mathrm{mol}$
c. $\quad 66.3 \mathrm{~kJ} / \mathrm{mol}$
d. $-127.94 \mathrm{~kJ} / \mathrm{mol}$
e. $\quad 127.94 \mathrm{~kJ} / \mathrm{mol}$

Biotites $\left(\mathrm{K}(\mathrm{Mg}, \mathrm{Fe})_{3} \mathrm{AlSi}_{3} \mathrm{O}_{10}(\mathrm{OH})_{2}\right)$ and garnets $\left((\mathrm{Mg}, \mathrm{Fe})_{3} \mathrm{Al}_{2} \mathrm{Si}_{3} \mathrm{O}_{12}\right)$ are well-known minerals that can be used to measure temperatures at which certain rock samples were formed (i.e. they are used as geothermometers). These minerals can exchange their iron and magnesium cations as expressed in the following equation:

$$
\mathrm{Fe}_{3} \mathrm{Al}_{2} \mathrm{Si}_{3} \mathrm{O}_{12}+\mathrm{KMg}_{3} \mathrm{AlSi}_{3} \mathrm{O}_{10}(\mathrm{OH})_{2}=\mathrm{Mg}_{3} \mathrm{Al}_{2} \mathrm{Si}_{3} \mathrm{O}_{12}+\mathrm{KFe}_{3} \mathrm{AlSi}_{3} \mathrm{O}_{10}(\mathrm{OH})_{2}
$$

This is a reversible process and its equilibrium constant is expressed in terms of mole fractions of magnesium and iron cations in each mineral.

|  | $\Delta \mathrm{H}^{\circ}, \mathrm{kJ} / \mathrm{mol}$ | $\mathrm{S}^{\circ}, \mathrm{J} / \mathrm{K} \cdot \mathrm{mol}$ |
| :--- | :---: | :---: |
| $\mathrm{Fe}_{3} \mathrm{Al}_{2} \mathrm{Si}_{3} \mathrm{O}_{12}$ | -5267 | 340 |
| $\mathrm{KMg}_{3} \mathrm{AlSi}_{3} \mathrm{O}_{10}(\mathrm{OH})_{2}$ | -6210 | 334 |
| $\mathrm{Mg}_{3} \mathrm{Al}_{2} \mathrm{Si}_{3} \mathrm{O}_{12}$ | -6287 | 266 |
| $\mathrm{KFe}_{3} \mathrm{AlSi}_{3} \mathrm{O}_{10}(\mathrm{OH})_{2}$ | -5142 | 421 |

The garnet sample contains $30.12 \% \mathrm{FeO}$ and $2.23 \% \mathrm{MgO}$ by mass, and the sample of biotite that was in equilibrium with the garnet contains $23.54 \% \mathrm{FeO}$ and $7.98 \% \mathrm{MgO}$ by mass. Calculate the temperature at which the sample was formed.
a. 524 K
b. 587 K
c. 673 K
d. 942 K
e. 1340 K

