1. Hydrogen hydrates are peculiar compounds that are produced by treating cooled ice with hydrogen at high pressure. Under standard conditions, they are thermodynamically unstable. For the following reaction,

$$xH_2(g) + H_2O(s) \longrightarrow (xH_2*H_2O)(s)$$
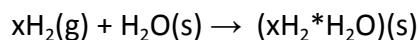
Determine the signs of $\Delta H, \Delta S, \Delta G$ **(in this order, left to right)**

    a. >0, <0, <0

    b. <0, <0, >0

    c. <0, =0, <0

    d. =0, <0, =0

    e. <0, >0, <0

Syngas (synthesis gas) is a mixture of hydrogen and carbon monoxide, usually obtained by steam reforming of natural gas:

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g)+3H_2(g)$$
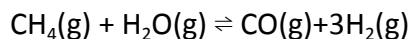
Consider this process for the questions 2 – 5.

2. Characterize the spontaneity of the reaction given $\Delta_r H^\circ$ = 205.8 kJ mol^{-1} and $\Delta_r S^\circ$ = 214.2 J mol^{-1} K^{-1}

    a. The reaction is always spontaneous

    b. The reaction is never spontaneous

    c. The reaction is spontaneous at very low temperatures

    d. The reaction is spontaneous at very high temperatures

    e. The spontaneity of the reaction cannot be determined from the information provided

3. What effect on the yield of syngas will be caused by the increase of pressure in a closed system?

    a. It would increase because the equilibrium would shift towards the products

    b. It would decrease because the equilibrium would shift towards the products

    c. It would increase because the equilibrium would shift towards the reactants

    d. It would decrease because the equilibrium would shift towards the reactants

    e. It would not change

4. What effect on the yield of syngas will be caused by the increase in temperature?

    a. It would increase because the equilibrium would shift towards the products

    b. It would decrease because the equilibrium would shift towards the products

    c. It would increase because the equilibrium would shift towards the reactants

    d. It would decrease because the equilibrium would shift towards the reactants

    e. It would not change

5. Calculate the equilibrium constant of this reaction at 300°C.

    a. $K_{eq} = 2.68 \times 10^{-8}$ d. $K_{eq} = 1.42 \times 10^{12}$

    b. $K_{eq} = 2.27 \times 10^{-25}$ e. $K_{eq} = 3.67 \times 10^{-18}$

    c. $K_{eq} = 1.48 \times 10^{11}$

6. The equilibrium constant K_c for the process $H_2 + I_2 \rightleftharpoons 2HI$ at a certain temperature is 40. Determine what percentage of hydrogen will turn into HI if the initial concentrations of these substances (both H_2, I_2 and HI) are the same and amount to 0.010 M.

    a. 48%   d. 76%

    b. 80%   e. 64%

    c. 86%
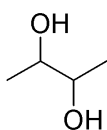
7. Which of the following compound is the most likely to react with nucleophiles?

    1   2   3   4   5

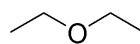   a. 1   d. 4

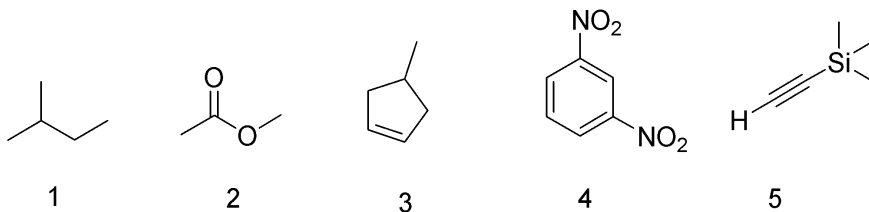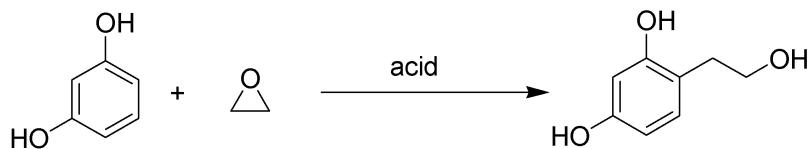   b. 2   e. 5

    c. 3
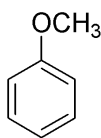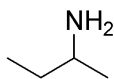
8. For which of the following compounds you would observe different numbers of signals in ^{13}C and ^1H NMR spectra?


    1   2   3   4   5

a. 1 and 3
b. 2 and 4
c. 2, 4 and 5

d. only 4
e. only 5

9. What is the type of the reaction given below?

a. rearrangement
b. electrophilic addition
c. nucleophilic addition

d. elimination
e. electrophilic substitution

10. The pinacol–pinacolone rearrangement is a method for converting a 1,2-diol to a carbonyl compound in acidic conditions. The key steps in the mechanism are the formation of a carbocation and a 1,2-migration of alkyl group:
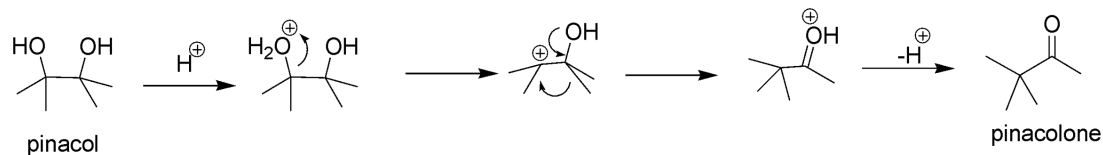
For the starting material given below predict the major product of the reaction:

a.

b.

c.

d.

e.
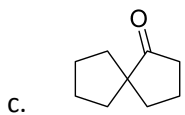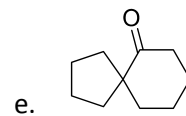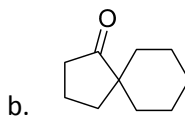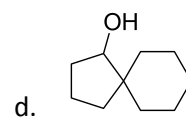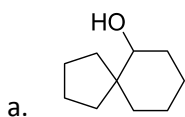
11. What is the main product of the reaction given below (the quantity in moles of bromine is equal to the quantity in moles of starting material)?

a. 3,4-dibromocyclohex-1-ene

b. 3,6-dibromocyclohex-1-ene

c. 1,2,3,4-tetrabromocyclohexane

d. 5-bromocyclohexa-1,3-diene

e. 1-bromocyclohexa-1,3-diene
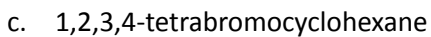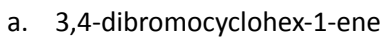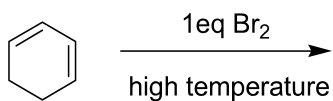
12. Which compound's water solution will have the lowest pH value?

1	2	3	4	5

   a. 1   d. 4

   b. 2   e. 5

   c. 3

13. Choose the correct oxidation number for each element in the complex salt $Na_3[Cr(OH)_6]$ (from left to right):

   a. +1, -3, -2, +1   d. +1, +6, -2, +1

   b. -1, +3, +2, -2   e. +1, +9, -3, +1

   c. +1, +3, -2, +1

14. In the following reaction, what are the oxidizing agent and the reducing agent

$$2ClO_2 + 2NaOH \rightarrow NaClO_2 + NaClO_3 + H_2O$$
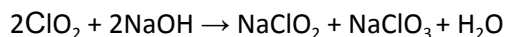
   a. $NaOH$, ClO_2 d. ClO_2, $NaClO_3$

   b. ClO_2, $NaOH$ e. ClO_2, ClO_2

   c. ClO_2, $NaClO_2$

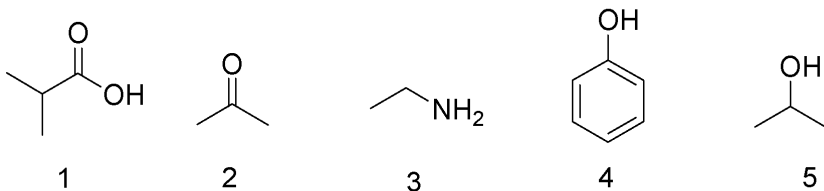15. The salts of metal X and their solutions tend to be vibrantly colored. Probably its famous compound with intensely purple water solution, containing X in highest oxidation state, is widely used both in inorganic and organic chemistry due to its oxidation properties. In media of different acidity, it is reduced to various oxidation states forming slightly pink solutions at low pH, dark brown or black precipitate at neutral pH, and deep green solutions at high pH. Name the metal X.

   a. Cr   d. Mn

   b. Ir   e. Bi

   c. S

In problems 16 – 18, where needed, use F = 96485 C mol^{-1}.

16. One half-cell in a voltaic cell at 60°C is constructed from lead wire dipped into a 0.65 M $Pb(NO_3)_2$ solution. The other half-cell consists of a cadmium electrode in a 0.24 M $Cd(NO_3)_2$ solution. Calculate the electromotive force (emf) of the cell.

    a. 0.270 V   d. 0.256 V

    b. 0.299 V   e. -0.284 V

    c. 0.284 V

17. Using standard reaction potentials, calculate the equilibrium constant (at standard conditions) of the given reaction:

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \rightleftharpoons 2MnSO_4 + 5Fe_2(SO_4)_3 + K_2SO_4 + 8H_2O$$

    a. $K_{eq} = 1.41 \times 10^{125}$ d. $K_{eq} = 2.67 \times 10^{-63}$

    b. $K_{eq} = 3.75 \times 10^{62}$ e. $K_{eq} = 3.27 \times 10^{35}$

    c. $K_{eq} = 3.27 \times 10^{12}$

18. A silver chloride electrode is a type of reference electrode, commonly used in electrochemical measurements. The equilibrium is between the solid silver metal and its solid low-soluble salt — silver chloride. The electrode is submerged in a chloride solution (usually an alkali chloride, such as KCl) of a given concentration.

The value of a standard reduction potential of this electrode directly follows from the half-reaction potential for silver (Ag^+/Ag) electrode and is determined for a solution with a concentration of Cl^- of 1 M.

Using Nernst equation, calculate the solubility product constant for AgCl.

    a. $K_{sp} = 1.90 \times 10^{-4}$ d. $K_{sp} = 2.95 \times 10^{-14}$

    b. $K_{sp} = 1.55 \times 10^{-10}$ e. $K_{sp} = 1.24 \times 10^{-5}$

    c. $K_{sp} = 6.44 \times 10^{9}$

19. Which of the following compounds is the best oxidizer at pH = 0?

    a. $KMnO_4$ d. VO_2NO_3

    b. PbO_2 e. $K_2Cr_2O_7$

    c. $Co(NO_3)_3$

20. Which of the following processes are spontaneous at standard conditions (25°C, 1 atm)?

$$2Au + 3F_2 \rightarrow 2AuF_3 \qquad\qquad (1)$$

$$SnCl_2 + Cu \rightarrow CuCl_2 + Sn \qquad\qquad (2)$$

$$Ag + ClO_2 \rightarrow AgClO_2 \qquad\qquad (3)$$

$$2HNO_3 + 3PbSO_4 + 2H_2O \rightarrow 2NO + 3H_2SO_4 + 3PbO_2 \qquad (4)$$
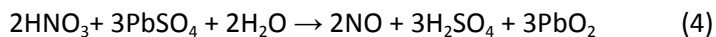
a. only 1

b. 1, 3 and 4

c. 2 and 4

d. 1 and 3

e. all of them

Use the information below for problems 21, 22 and 23.

Rate of chemical reactions can be expressed in a general form as

$$rate = k\,[reactant_1]^m[reactant_2]^n \ldots$$

where **k** is a constant dependent on temperature. Powers **m** and **n** (and following) to which the concentrations of reactants are raised are simply equal to stoichiometric coefficients for the case of so-called *elementary reactions*. These powers are called *orders in a specific reactant* and their sum is overall *reaction order*.

21. The decomposition reaction $2HI(g) = H_2(g) + I_2(g)$ is of 2nd order with a rate constant $k = 5.95 \times 10^{-6}\,L\,mol^{-1}\,s^{-1}$. Calculate the initial reaction rate at a pressure of 1 atm and a temperature of 600 K. Consider

a. $2.45 \times 10^{-3}\,mol\,L^{-1}\,s^{-1}$

b. $1.21 \times 10^{-7}\,mol\,L^{-1}\,s^{-1}$

c. $9.95 \times 10^{-9}\,mol\,L^{-1}\,s^{-1}$

d. $1.21 \times 10^{-3}\,mol\,L^{-1}\,s^{-1}$

e. $2.45 \times 10^{-9}\,mol\,L^{-1}\,s^{-1}$

22. The rate of a gas-phase reaction is given by the equation $r = k[A]^2[B]$. At what ratio between the concentrations of A and B will the initial reaction rate be maximum at a fixed total pressure?

a. [A]:[B] = 2:1

b. [A]:[B] = 1:1

c. [A]:[B] = 1:2

d. [A]:[B] = 4:1

e. [A]:[B] = 1:16

23. By how many times and in what direction would the rate of the gas-phase elementary reaction A = 2D change if the pressure increased by 3 times?

a. It wouldn't change

b. It would decrease by 3 times

c. It would increase by 3 times

d. It would decrease by 9 times

e. It would increase by 9 times

24. Calculate the boiling point of elemental bromine (which is defined as a temperature at which the evaporation becomes spontaneous), if for the following process:

$$Br_2(l) \rightarrow Br_2(g)$$
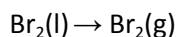
the $\Delta_rH° = 30.9$ kJ mol^{-1} and $\Delta_rS° = 93$ J mol^{-1} K^{-1}

a. 59°C

b. 332°C

c. 93°C

d. 3°C

e. 146°C

25. Among the processes below, which are exothermic?

Sublimation of dry ice	(1)
Dehydrating sodium sulfate decahydrate	(2)
Burning of wood in a fireplace	(3)
Reaction of sodium hydroxide with hydrochloric acid	(4)
Freezing of liquid ammonia	(5)

a. 1 and 2

b. 3, 4 and 5

c. 1, 3 and 4

d. 3 and 4

e. only 3

26. Which statement is true for any spontaneous process we are investigating?

a. Entropy of the universe increase

b. Entropy of the universe decrease

c. Entropy of the universe stays the same

d. Entropy of the system increases

e. Entropy of the system stays the same

27. From the reaction coordinate diagram, determine if the reaction is exo- or endothermic and how the energy of activation and enthalpy of the reaction compares?
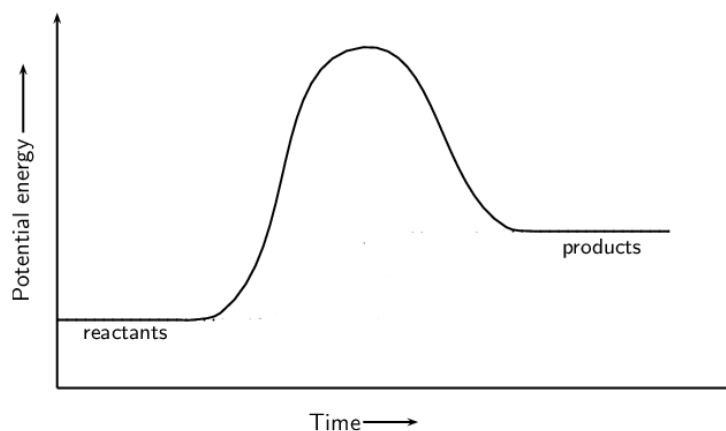
a. The reaction is exothermic and $\Delta H > E_a$

b. The reaction is endothermic and $\Delta H > E_a$

c. The reaction is exothermic and $\Delta H < E_a$

d. The reaction is endothermic and $\Delta H < E_a$

e. The reaction is endothermic and $\Delta H = E_a$

28. Nitrogen dioxide can reversibly decompose to form nitrogen monoxide and elemental oxygen via the reaction:

$$2NO_2 \rightleftharpoons 2NO + O_2$$
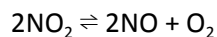
The equilibrium constant of this reaction equals to 0.119 at 700 K and 9.39 at 900 K.
In what direction (direct or reverse) will the reaction proceed at both temperatures, if the mixture contains 0.15 M NO_2, 0.33 M NO, 0.080 M O_2.

a. Direct at 700 K, reverse at 900 K

b. Direct at 700 K, direct at 900 K

c. Reverse at 700 K, reverse at 900 K

d. Reverse at 700 K, direct at 900 K

e. The directions cannot be determined from the information provided

29. Enthalpy and entropy of any reaction can be calculated from entropies and enthalpies of formation of reactant and products. For example, for a general reaction:
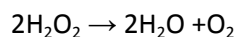
$$aA + bB \rightarrow cC + dD$$
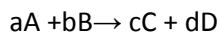
$\Delta_r H° = c \times \Delta_f H°(C) + d \times \Delta_f H°(D) - a \times \Delta_f H°(A) - b \times \Delta_f H°(B)$
$\Delta_r S° = c \times S°(C) + d \times S°(D) - a \times S°(A) - b \times S°(B)$

Standard molar enthalpies of formation of homonuclear compounds in their most stable allotropic forms (Cl_2 (g), N_2 (g), Br_2 (l) etc.) is equal to zero.
Calculate $\Delta_r G°$ (at 25°C) for the reaction below:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

given that $\Delta_f H°(H_2O_2)$ = -191.4 kJ mol^{-1}, $\Delta_f H°(H_2O)$ = -187.8 kJ mol^{-1},
$S°(H_2O_2)$ = 142.4 J mol^{-1} K^{-1}, $S°(H_2O)$ = 100.5 J mol^{-1} K^{-1}, $S°(O_2)$ = 205.04 J mol^{-1} K^{-1}.

   a. $\Delta_r G°$ = -45 kJ mol^{-1}
         d. $\Delta_r G°$ = -41 kJ mol^{-1}

   b. $\Delta_r G°$ = -33 kJ mol^{-1}
         e. $\Delta_r G°$ = 33 kJ mol^{-1}

   c. $\Delta_r G°$ = -29 kJ mol^{-1}

30. Calculate the solubility (in M) of lead (II) iodide in water at 20°C if its solubility product (equilibrium constant for the process of dissolution) at these conditions is equal to 4.41×10^{-9}.
   a. 4.41×10^{-9} M
         d. 1.64×10^{-3} M

   b. 1.03×10^{-3} M
         e. 6.64×10^{-5} M

   c. 3.32×10^{-5} M

Supporting Information

Standard Reduction Potentials at 25°C (298 K) for Many Common Half-reactions

Half-reaction	$\mathscr{E}°$ (V)	Half-reaction	$\mathscr{E}°$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$IO_4^- + 2H^+ + 2e^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	-0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	-0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	-0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	-1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	-1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	-2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	-2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	-2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	-2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	-2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	-2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	-3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

Useful equations:

Relationship between equilibrium constant, Gibbs energy and enthalpy and entropy:

$$ - RTlnK_{eq} = \Delta G = \Delta H - T\Delta S$$

Nernst equation for electrochemical half-cell:

$$E = E^o + \frac{RT}{zF}\ln ln \frac{[Ox]}{[Red]}$$

Electromotive force:

$$Emf = - \frac{\Delta G}{zF}$$