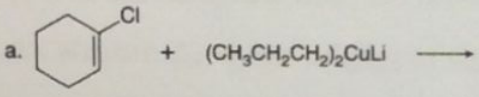
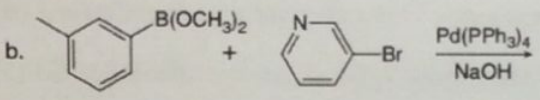
1. The standard enthalpy change for the reaction

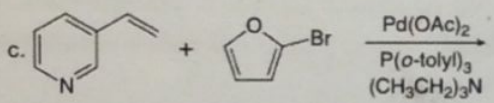
$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$$

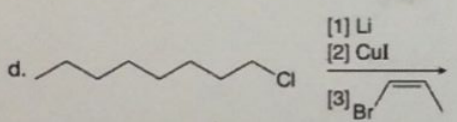
is -571.6 kJ mol^{-1} at 25 °C. Calculate the value of ΔH°_{rxn} at 100 °C, assuming that all molar C_p^o values are independent of temperature. (Molar C_p^o is 29.4, 28.8, and 75.3 J mol^{-1} K^{-1} for $O_2(g)$, $H_2(g)$, and $H_2O(l)$, respectively.)

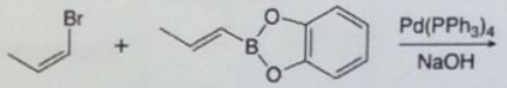
2. Draw the products formed in each reaction.1

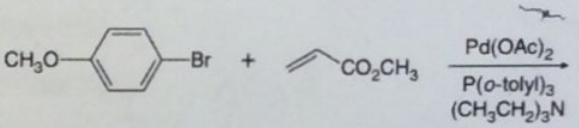
a. 

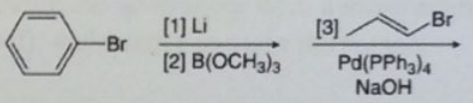
b. 

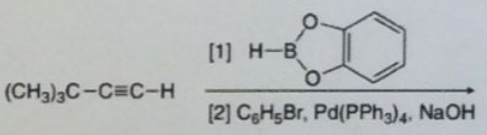
c. 

d. 

e. 

f. 

g. 

h. 

3. Iron has a heat capacity of 25.1 J $K^{-1}mol^{-1}$, approximately independent of temperature between 0 °C and 100 °C.

(a) Calculate the enthalpy and entropy change of 1.00 mol iron as it is cooled at atmospheric pressure from 100 °C to 0 °C.

(b) A piece of iron weighting 55.85 g and at 100 °C is placed in a large reservoir of water held at 0 °C. It cools irreversibly until its temperature equals that of the water. Assuming the water reservoir is large enough that its temperature remains close to 0 °C, calculate the entropy changes for the iron and the water and the total entropy change in this process.

4.

(a) Calculate *q, w, ΔH, and ΔU* for the following reaction. (Assume that the gas behaves ideally and that the volume occupied by the liquid is negligible.)

2.00 mol NH_3 (*l*, 1 atm, 240 K) → 2.00 mol NH_3 (*g*, 1 atm, 298 K)

- Normal boiling point of liquid ammonia: 240 K
- Enthalpy of vaporization at 240 K: 23.4 kJ mol^{-1}
- C_p of ammonia: 38 J $K^{-1}mol^{-1}$

(b) Calculate the entropy of vaporization of ammonia at 240 K.

5. In the following reaction,

$$PCl_3(g) + Cl_2(g) \rightleftarrows PCl_5\ (g)\ K = 0.56\ (L\ mol^{-1}) \text{ at } 250\ °C$$

1.50 mol PCl_5, 3.00 mol PCl_3, 0.50 mol Cl_2 are present in a 0.500 L reaction vessel at 250 °C [$\Delta H_f°(PCl_3(g)) = -287.0$ kJ mol^{-1}, $\Delta H_f°\ (PCl_5(g)) = -374.9$ kJ mol^{-1}].

(a) Is the reaction at equilibrium? Write the reason for your statement.

(b) If not, in which direction is it proceeding?

(c) What are the equilibrium compositions (mol L^{-1}) of all chemical substances?

(d) Once the equilibrium is reached, if the temperature is increased to 300 °C, do you expect more chlorine gas to be consumed or generated?

(e) Once the equilibrium is reached, if you compress the vessel to half the volume, do you expect more chlorine gas to be consumed or generated?

6. The vapor pressure of ammonia at −50 °C is 0.4034 atm. At 0 °C, it is 4.230 atm. Assume that ΔH_{vap} and ΔS_{vap} are approximately independent of temperature.

(a) Calculate the molar enthalpy of vaporization of ammonia.

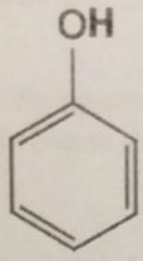
(b) Calculate the molar entropy of vaporization of ammonia.

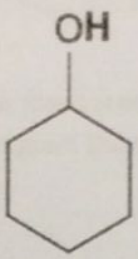
$K = P(NH_3)$

(c) Calculate the normal boiling temperature of ammonia liquid. $\Delta G = 0$

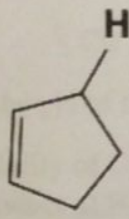
7. Between two chemical structures shown below, circle the substances with a more acidic proton (evaluate the acidity of the "**bold**" protons, a-f), and briefly explain the reason.

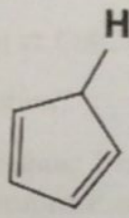
(a)





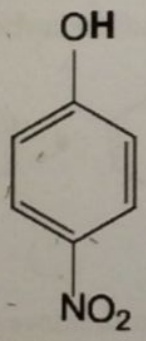
(b)

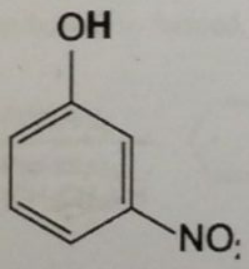




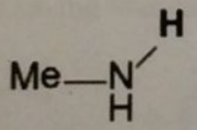
(c) CF_3COOH CCl_3COOH

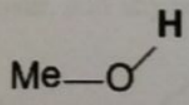
(d)



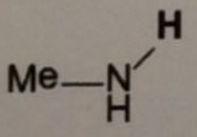


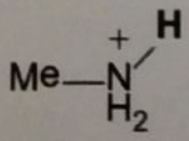
(e)





(f)





8.

Find the pH of acetic acid (HA)/ sodium acetate (NaA) buffer solutions made from

(a) 50 mL 0.20 M HA and 50 mL 0.20 M NaA

(b) 25 mL 0.20 M HA and 75 mL 0.20 M NaA.

(c) Calculate the change in pH when 80 mg NaOH (s) is added to each of these solutions (a and b).

(d) Compare the results with adding the same amount of NaOH to an unbuffered solution of the same pH and volume as solution (a). Neglect the change in volume on adding NaOH (s) (pK_a of HA is 4.75).

9.

(a) Calculate the concentration of Cu^{2+} (aq) in an aqueous solution that contains 0.020 ml of $CuCl_2$ and 0.1 mol of NaCN in 1.0 L (pK_a of HCN is 9.21).

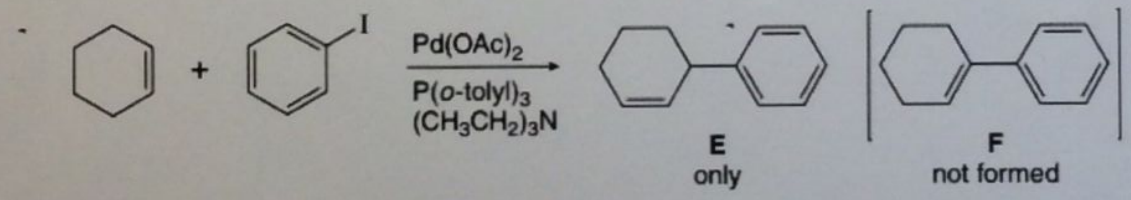
$$Cu^{2+}(aq) + 4CN^{-}(aq) \rightleftarrows Cu(CN)_4^{2-}(aq) \qquad K_f = 2.0 \times 10^{30}$$

(b) What is the pH of the resulting solution?

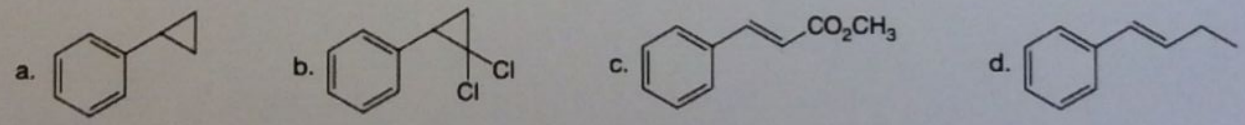
10. The solubility of $CaCO_3$ in water is about 7 mg L^{-1}. Show how one can calculate the solubility product of $BaCO_3$ from this information and from the fact that when sodium carbonate solution is added slowly to a solution containing equimolar concentrations of Ca^{2+} and Ba^{2+}, no $CaCO_3$ is formed until about 90% of the Ba^{2+} has been precipitated as $BaCO_3$.

11.

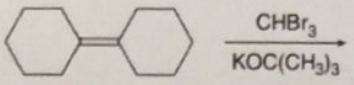
(a) The reaction of cyclohexene with iodobenzene under Heck conditions forms **E,** a coupling product with the new phenyl group on the allylic carbon, but none of the "expected" coupling product **F** with the phenyl group bonded directly to the carbon–carbon double bond. Draw a stepwise mechanism that illustrates how **E** is formed.

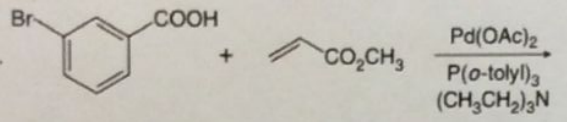


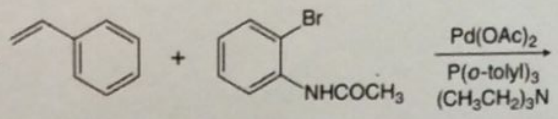
(b) Devise a synthesis of each compound from benzene. You may also use any organic compounds having four carbons or fewer, and any required inorganic reagents.

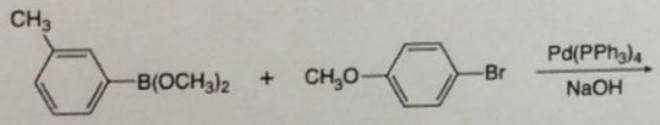


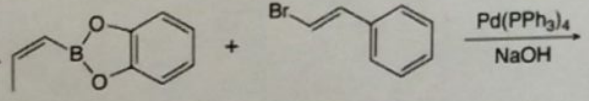
12. Draw the products formed in each reaction.

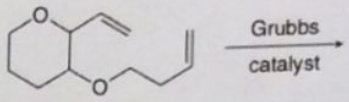
a. 

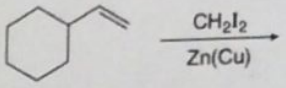
b. 

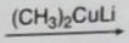
c. 

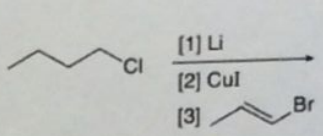
d. 

e. 

f. 

g. 

h. The product in (a) 

i. 

j.