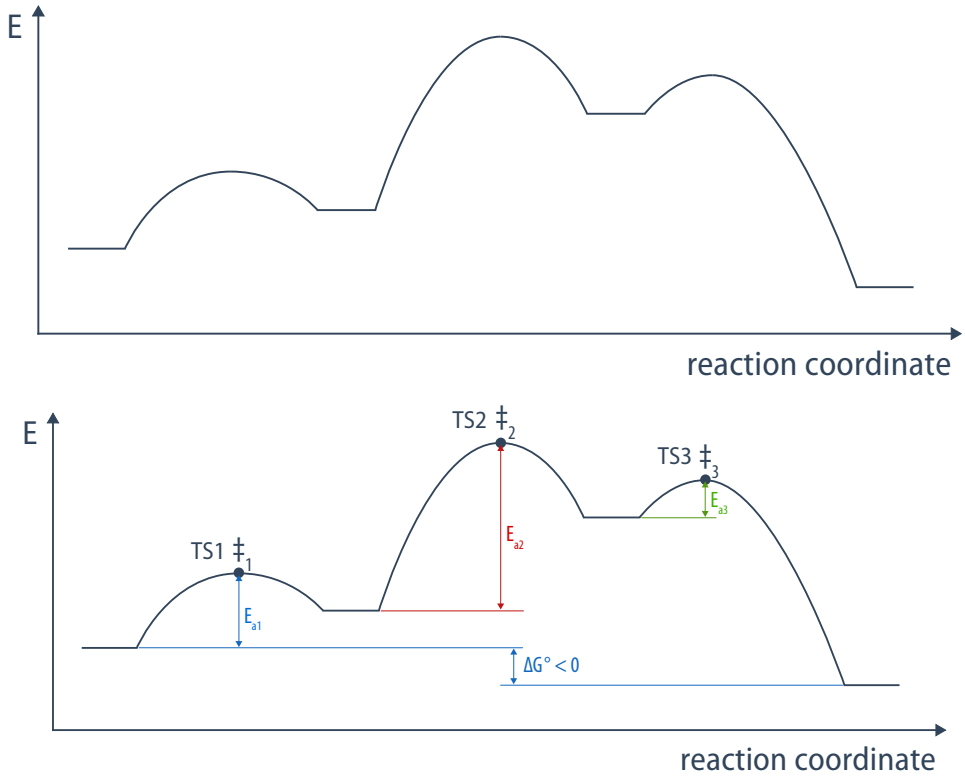
Organic Chemistry – Exercise 5

Distribution: October 30, 2025

Help: November 6, 2025

Return until: November 8, 2025

1. Consider the given profile of a chemical reaction.



   a. Label ΔG° on the diagram. Is its value positive or negative for this reaction? Is the reaction spontaneous or not?

      The value of ΔG° is negative, so the reaction is spontaneous.

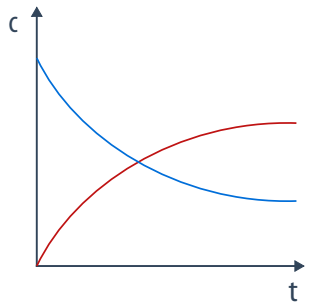
   b. How many elementary steps are there in the mechanism of this reaction? Label all the transition states on the diagram.

      There are 3 elementary steps and 3 transition states.

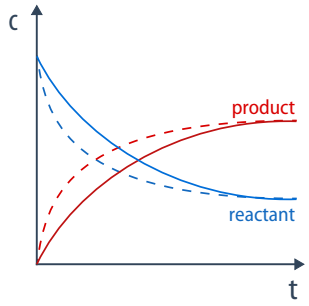
   c. Which step is the rate determining step? Explain why.

      The second step is the rate determining step. The rate determining step is the slowest one, as it has the highest activation energy (check Arrhenius equation).

   d. The concentration of one of the reactants and one of the products were followed over a period of time. The following dependences of species concentration on time were observed. Which curve corresponds to the concentration of the reactant and which one corresponds to the concentration of the product? Sketch the concentration dependence for the same reaction if a catalyst is introduced in the system.



As the reactant is being consumed during the reaction, its concentration is decreasing over time, so the blue curve corresponds to the reactant. As the product is being produced during the reaction, its concentration is increasing over time, so the red curve corresponds to the product. Adding the catalyst affects ONLY the rate constant and it speeds up the process (final concentrations are reached after a shorter time). The starting and the ending concentrations must be the same.



2. Consider the given chemical reaction.

a. Give the IUPAC names of the reactants and the product. Include stereochemical information.

Reactants: (*E*)-but-2-ene and water; Product: (*R*)-butan-2-ol and (*S*)-butan-2-ol

b. What is the reaction type?

This is an addition reaction.

The standard enthalpy and entropy of this reaction are, respectively, $\Delta H° = -44$ kJ mol^{-1} and $\Delta S° = -120$ J K^{-1} mol^{-1}.

c. Is this reaction endothermic or exothermic?

The enthalpy is negative, so the reaction is exothermic.

d. Is this reaction spontaneous at room temperature?

Using Gibbs-Helmholtz equation, the reaction Gibbs energy is $\Delta G° = \Delta H° - T\,\Delta S° = -8.22$ kJ mol^{-1}, so the reaction is spontaneous at room temperature.

e. Calculate the equilibrium constant for this reaction at room temperature.

As $\Delta G° = -8.22$ kJ mol^{-1} and $\Delta G° = -RT \ln K_{eq}$, so $K_{eq} = 27.6$.

f. What is the highest temperature at which this reaction can be carried out?

The reaction is spontaneous as long as $\Delta G° < 0$, so the maximum temperature can be found from the Gibbs-Helmholtz equation using the condition $\Delta G° = \Delta H° - T\,\Delta S° < 0$. The reaction is spontaneous until $T = 366.6$ K ($T = 93.5$ °C).

3. Ammonia is industrially synthesized through the Haber-Bosch process. The reaction enthalpy is $\Delta H° = -92.3$ kJ mol^{-1} and the reaction entropy is $\Delta S° = -198.5$ J K^{-1} mol^{-1}.

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$

This process is carried out in the presence of a solid catalyst, containing wüstite, aluminium oxide, potassium oxide, calcium oxide, magnesium oxide and molybdenum, under high pressure (60–180 bar) and at elevated temperature (300–500 °C).

a. Calculate the equilibrium constant at 400 °C.

As $\Delta G° = \Delta H° - T\,\Delta S°$ and $\Delta G° = -RT \ln K_{eq}$, $K_{eq} = 6.22 \cdot 10^{-4}$. (Note: Don't forget to convert the temperature to Kelvin!)

b. **Bonus question:** Even though the reaction is exothermic, it is performed at elevated temperatures. What could be the reason for this?

At lower temperatures, the gas molecules have lower speed, meaning that the probability of collision is lower. In order to increase the collision probability, the reaction is performed at higher temperature.

c. If a reactor with the volume of $V = 1$ dm^3 is loaded with 50 mol of N_2, 50 mol of H_2 and 50 mol of NH_3, will the reaction proceed in the direction of ammonia production or consumption? Consider the temperature to be 400 °C.

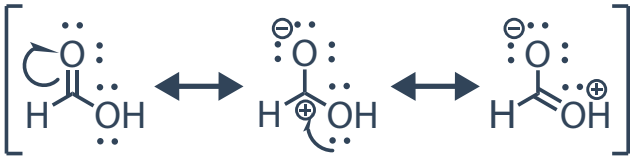
If we calculate the concentration product for the given system, the value of $Q = 4 \cdot 10^{-4}$ is obtained. As this value is smaller than the value of the equilibrium constant at this temperature, the reaction will proceed in the direction of ammonia production.

d. If the system described in the previous point is allowed to reach equilibrium, calculate the equilibrium concentrations of nitrogen, hydrogen and ammonia. *Hint*: if you are not familiar with numerical solving of equations, you can use online solvers to solve the polynomial equation that you will get.

Due to the stoichiometric coefficients, the final concentrations can be labeled as $[H_2] = 50 - 3x$ mol dm^{-3}, $[N_2] = 50 - x$ mol dm^{-3} and $[NH_3] = 50 + 2x$ mol dm^{-3}. When these values are put into the expression for the equilibrium constant and the polynomial equation is solved, the result is $x = 1.54$ mol dm^{-3}. Now, the equilibrium concentrations are $[H_2] = 45.38$ mol dm^{-3}, $[N_2] = 48.46$ mol dm^{-3} and $[NH_3] = 53.08$ mol dm^{-3}.

4. Formic acid (methanoic acid) can act as both a nucleophile and an electrophile.

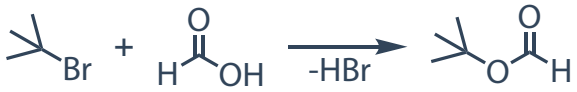
a. Show three resonance structures of formic acid.



b. Based on its structure, explain why formic acid can act as both a nucleophile and an electrophile.

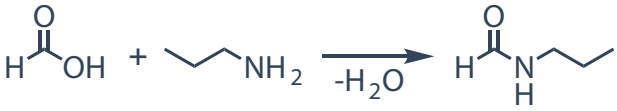
The carbon atom has partial positive charge and can act as an electrophilic center. On the other hand, the oxygen atom has partially negative charge and can act as a nucleophile.

c. This is a reaction between *tert*-butyl bromide and formic acid. What is the reaction type? Is formic acid acting as a nucleophile or an electrophile in this reaction?



This is a substitution reaction. Formic acid is acting as a nucleophile.

d. This is a reaction between formic acid and propan-1-amine. What is the reaction type? Is formic acid acting as a nucleophile or an electrophile in this reaction?



This is a substitution reaction. Formic acid is acting as an electrophile.

5. In acidic medium, 4-hydroxybutanal forms a cyclic hemiacetal. The reaction is shown below.

a. What is the reaction type? Which group is acting as a nucleophile and which is acting as an electrophile?

This is an addition reaction. The hydroxyl group (O atom) acts as a nucleophile and the carbonyl group (C atom) acts as an electrophile.

b. Label all chiral centers in the starting compound and the product with an asterisk.

Reading Suggestions:

Clayden, Greeves, Warren, *Oxford University Press*, **2012**.

Organic Chemistry, John McMurry, *Thomson Brooks/Cole*, **2008**.

Chimie Organique, Les Grands Principes, John McMurry, *Dunod Editeur*, **2009**.

Chimie Organique, Paul Arnaud, *Dunod Editeur*, **2009**.