

Hydrodesulfurization

7% of total							
Question	5.1	5.2	5.3	5.4	5.5	5.6	Total
Points	2.5	3	3.5	5	8	12.5	34.5
Score							

The production of sulfur-free fuels is the general trend towards lowering the emission of sulfur-containing compounds that are toxic to the environment. To remove sulfur, the hydrogen-assisted hydrodesulfurization process is used at the refineries.

- 5.1** Draw the structure of products **A** to **E** of thiophene hydrodesulfurization, knowing that **A** and **B** are cyclic regioisomers and **C** is cyclic. 2.5pt

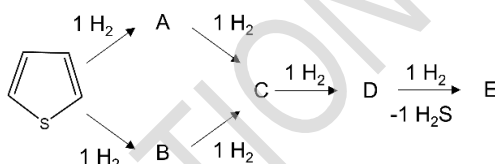


Figure 1. Thiophene hydrodesulfurization process.

Sulfur has two most common natural stable isotopes, ^{32}S and ^{34}S , with a relative molar abundance of $\chi(^{32}\text{S}) = 94.8\%$ and $\chi(^{34}\text{S}) = 4.37\%$, respectively. For hydrogen, the stable natural isotopes are ^1H and $^2\text{H}(\text{D})$, with a relative molar abundance of $\chi(^1\text{H}) = 99.986\%$ and $\chi(^2\text{H}) = 0.014\%$, respectively.

- 5.2** Considering only the isotopes listed above, **list** all isotopologues of H_2S . 3pt

- 5.3** Considering only the isotopes listed above, **list** all isotopologue of H_2S containing simultaneously D and ^{34}S nuclei and for each **calculate** the respective relative molar abundance in %.

The desulfurization is a catalytic process typically carried out over MoS_2 supported on SiO_2 ($\text{MoS}_2/\text{SiO}_2$) catalyst. To study the surface of the catalyst, isotope exchange methods can be employed. The isotope exchange reaction takes place at the gas-solid interface, resulting in the exchange of the surface atoms exclusively. In a first approximation, the bulk atoms do not participate in the exchange (**Figure 2**).

In the experiment, the isotope exchange between the $\text{MoS}_2/\text{SiO}_2$ catalyst (Mo mass fraction $w_{\text{Mo}} = 4.280 \text{ wt.}\%$, initially containing only ^{32}S) and gaseous isotopically-labeled H_2^{34}S was studied in a flow reactor (**Figure 2**). The $\text{MoS}_2/\text{SiO}_2$ catalyst ($m_{\text{cat}} = 1.2350 \text{ g}$) was kept in a flow ($p = 1.00 \text{ bar}$, $v = 20.0 \text{ mL min}^{-1}$, $T = 23.0 \text{ }^\circ\text{C}$) of gas mixture containing H_2^{34}S balanced with Ar (volume fraction $\phi_{\text{H}_2^{34}\text{S}} = 1.00 \text{ vol.}\%$, ^{34}S isotopic purity $\alpha = 99.95 \text{ mol.}\%$).

The experiment duration was $t = 10.0$ min and gas from the outlet was collected during the entire experiment. The measured fraction of ^{34}S isotope among the sulfur atoms (γ) in the collected gas phase was $\gamma = 87.3$ mol.%. Assume ideal gas behavior, and that the elemental (not isotopic!) composition of MoS_2 on the surface and in the bulk are identical, and by the end of the experiment all sulfur atoms from the surface are exchanged with the gas phase.

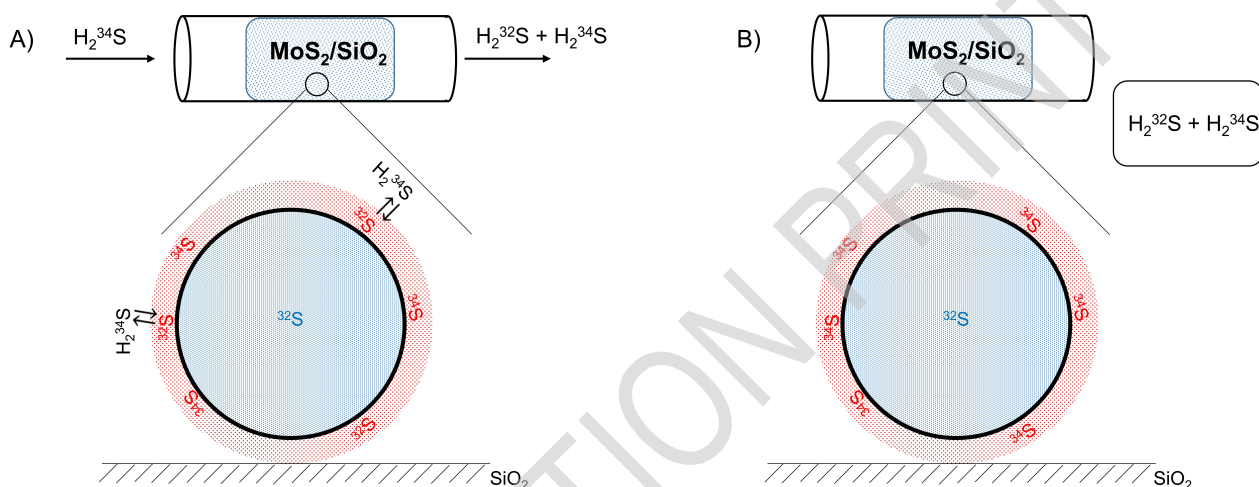


Figure 2. Schematic representation of the experiment in the course (A) and at the final stage (B). Sulfur atoms on the surface are shown in red, sulfur atoms in the bulk are shown in blue. Molybdenum atoms are not shown.

5.4 Calculate the number of exchanged sulfur atoms $n(S)_{\text{surface}}$, give your answer 5pt in mol.

If you have been unable to calculate the number of total exchanged sulfur atoms, use the value $1.53 \cdot 10^{-5}$ mol in all the following calculations.

Assume that the MoS_2 phase consists of uniform spherical particles, and at the end of the experiment all sulfur atoms located on the surface are exchanged, while the bulk atoms did not participate in the exchange reaction. The density ρ of MoS_2 is $\rho = 5.06$ g cm^{-3} , the average area occupied by S and Mo atoms on the surface is equal to $A_{\text{S}} = 3.00 \cdot 10^{-19}$ m^2 and $A_{\text{Mo}} = 5.00 \cdot 10^{-19}$ m^2 , respectively. The area of a sphere with radius R can be calculated as $S = 4\pi R^2$, and its volume as $V = \frac{4}{3}\pi R^3$. Assume that isotopic composition does not affect the density of MoS_2 .

5.5 Calculate the particle radius R of the MoS_2 particles, give your answer in nm. 8pt

In reality, the isotopically-labeled atoms from the surface diffuse into the bulk and the non-labeled atoms from the bulk travel to the surface, undergoing a gradual exchange (**Figure 3A**). Therefore, for a given moment, the fraction of the labeled atoms inside the particle decreases from the surface of the particle to its center. Simultaneously, with an increase in time of exchange, the involvement of bulk atoms to the exchange reaction increases, as sketched in **Figure 3B**.

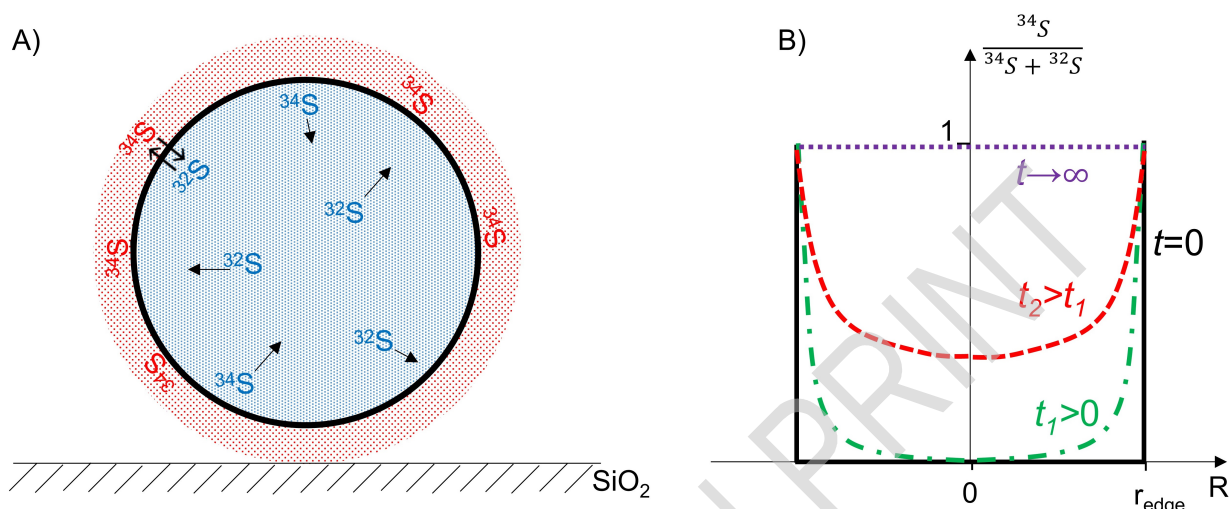


Figure 3. **A)** Schematic representation of the diffusion of sulfur isotopes from the surface to the bulk in MoS_2 particle. Sulfur atoms on the surface are shown in red, sulfur atoms in the bulk are shown in blue. Molybdenum atoms are not shown. **B)** The fraction of ^{34}S atoms in the bulk as function of time and distance from center of the particle. r_{edge} corresponds to the radius of MoS_2 particle.

At the end of the experiment, the surface atoms are completely exchanged, and additionally a fraction of the bulk is exchanged due to the diffusion. The fraction F of the exchanged bulk atoms ($n(S)_{\text{bulk}}^{\text{ex}}$) and the total bulk atoms of sulfur ($n(S)_{\text{bulk}}^{\text{total}}$) can be calculated as follows: $F = n(S)_{\text{bulk}}^{\text{ex}} / n(S)_{\text{bulk}}^{\text{total}} = 1 - e^{-\frac{D \cdot t}{R^2}}$, where t is the time of exchange experiment (described above), R is the particle size (radius for a spherical shape particle) and D is the diffusion coefficient. The catalyst described above was independently studied by means of electron microscopy, which showed that the MoS_2 particles are uniformly distributed spheres with a radius of 35.0 nm.

- 5.6** Using $R = 35.0$ nm as the radius and the data of the exchange experiment described above, **calculate** the diffusion coefficient D for the diffusion of sulfur atoms in MoS_2 , give your answer in $\text{m}^2 \text{s}^{-1}$. In your calculations, use the following approximation: $e^x \approx 1 + x$ for $x \ll 1$. 12.5pt