

Section 1. Write the phrases corresponding to the blanks in your answer sheet.

1. In a catalytic converter operating at low air-fuel ratio, the reaction _____ is promoted by the presence of _____ which serves as a source of _____.
2. The reaction happening at the anode of a fuel cell is _____. The anode and cathode are separated by a _____ made of _____.
3. The enzyme _____ is common to both the detergent and sweetener industry because in both cases _____. The form of the enzyme used in the food industry is _____ while the detergent one is not.
4. The active catalytic center in the heterogeneous polymerization catalyst is a _____-ion of which one Cl-atom is replaced by _____ while an adjacent Cl-atom has been completely removed in order to accommodate _____.
5. The common catalyst in steam-reforming reactions is _____. In addition to coke, it is readily poisoned by _____ which is removed by treatment with _____.
6. The Haber-Bosch process is conducted at _____ pressure with _____ as the catalyst and _____ as promoter.
7. The accepted mechanism for catalytic cracking involves a _____ ion which is created by _____ sites present in the _____ catalyst that is used.
8. If a _____ photoresist is used during _____, the portion that is exposed to light becomes _____ (soluble/insoluble).
9. The two main reactions in the Fischer-Tropsch process are _____ and _____.
10. If a reactant is either very strongly or weakly adsorbed on a catalytic surface, the catalytic activity will be _____. This is because if the adsorption is strong _____, while if it is weak _____.

Section 2. Short answers

1. The first order reaction $A(g) \longrightarrow A(\text{ads}) \longrightarrow B(g)$ has a rate of $1.8 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$ on a surface with dimensions 1.00 cm by 3.50 cm. How would the rate of the reaction change if the dimensions of the two sides of the surface were each doubled? How do you reconcile your conclusion with the interest in nanoscale materials for catalytic purposes?

Consider the reaction $2\text{CO}(g) + \text{O}_2(g) \longrightarrow 2\text{CO}_2(g)$ on a surface of platinum. It is known that on this surface, O_2 adsorbs dissociatively, while CO adsorbs molecularly.

2. Write a Langmuir-Hinshelwood (LH) mechanism for this reaction. Obtain the rate law if the adsorption steps are instantaneously at equilibrium.
3. If the reaction proceeds via an Eley-Rideal (ER) mechanism then $v = \frac{k_3 b_{\text{CO}} b_{\text{O}_2}^{1/2} P_{\text{CO}} P_{\text{O}_2}^{1/2}}{1 + b_{\text{O}_2}^{1/2} P_{\text{O}_2}^{1/2} + b_{\text{CO}} P_{\text{CO}}}$. Plot the prediction of the two models, the rate expression that you derived in question (2) and the ER expression above, as a function of the partial pressure of CO(g) at a fixed pressure of $\text{O}_2(g)$. (Hint: Obtain the limiting forms of the two expressions at low and high CO partial pressures.)

The energy of adsorption, E_{ads} , can be measured by a technique called temperature programmed desorption (TPD). In a TPD experiment, the temperature, (T) , of the surface with bound adsorbate is changed according to the equation $T = T_0 + \alpha t$, where T_0 is the initial temperature, α is a constant that determines the rate at which the temperature is changed, and t is the time. A mass spectrometer is used to measure the concentration of molecules that desorb from the surface. The analysis of TPD data depends on the kinetic model of desorption. Consider a first order desorption process $M-S(s) \xrightarrow{k_d} M(g) + S(s)$.

4. Write an expression for the rate law for desorption and then show that

$$\frac{d[\text{M-S}]}{dT} = -\frac{[\text{M-S}]}{\alpha} \left(\tau_0^{-1} e^{-E_{\text{ads}}/RT} \right).$$

Here τ_0 is the vibrational lifetime.

5. With increasing T , $\frac{d[\text{M-S}]}{dT}$ initially increases, then reaches a maximum, after which it decreases. Let $T = T_{\text{max}}$ be the temperature corresponding to the maximum rate of desorption. Show that $\frac{E_{\text{ads}}}{RT_{\text{max}}} = \frac{\tau_0^{-1}}{\alpha} e^{-E_{\text{ads}}/RT_{\text{max}}}$. Remember that $[\text{M-S}]$ is a function of temperature.
6. The equation in question 5 can be written as

$$2 \ln T_{\text{max}} - \ln \alpha = \frac{E_{\text{ads}}}{RT_{\text{max}}} + \ln \frac{E_{\text{ads}}}{R\tau_0^{-1}}.$$

Suggest how you would use this equation to determine τ_0 and E_{ads} .

7. On heating Cs vapor a small amount of Cs_2 is formed. Absorption of light around 620–680 nm excites Cs_2 molecules from the ground $X^1\Sigma_g^+$ state to the $C^1\Pi_u$ state. The latter state is photoionized on absorbing light of 615–628 nm giving detectable signal. All the relevant states are well-represented by Morse potentials. Show the relevant states on a potential energy diagram and explain how you would conduct a femtosecond pump-probe experiment to study the dynamics of Cs_2 in the $C^1\Pi_u$ state.
8. With the help of a series of diagrams of the potential energy surface along components of the collective reaction coordinate, show the effect of heavy-atom motions on the zero-point energy in the reactant and product potential well for Marcus-like model of H-tunneling. Identify the reorganization energy and the driving force on the diagram.

Answer Key for Exam A

Section 1. Write the phrases corresponding to the blanks in your answer sheet.

1. In a catalytic converter operating at low air-fuel ratio, the reaction water-gas shift reaction is promoted by the presence of ceria which serves as a source of oxygen.
2. The reaction happening at the anode of a fuel cell is $\frac{1}{2}\text{H}_2 \longrightarrow \text{H}^+ + \text{e}$. The anode and cathode are separated by a proton exchange membrane made of Nafion.
3. The enzyme amylase is common to both the detergent and sweetener industry because in both cases starch has to be hydrolysed. The form of the enzyme used in the food industry is thermally stable while the detergent one is not.
4. The active catalytic center in the heterogeneous polymerization catalyst is a Ti-ion of which one Cl-atom is replaced by an alkyl group R while an adjacent Cl-atom has been completely removed in order to accommodate the monomer molecule.
5. The common catalyst in steam-reforming reactions is nickel. In addition to coke, it is readily poisoned by sulphur which is removed by treatment with zinc oxide.
6. The Haber-Bosch process is conducted at high pressure with iron as the catalyst and KOH as promoter.
7. The accepted mechanism for catalytic cracking involves a non-classical carbonium ion which is created by acidic sites present in the zeolite catalyst that is used.
8. If a positive photoresist is used during photolithography, the portion that is exposed to light becomes soluble (soluble/insoluble).
9. The two main reactions in the Fischer-Tropsch process are $n\text{CO} + (2n + 1)\text{H}_2 \longrightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O}$ and $n\text{CO} + 2n\text{H}_2 \longrightarrow \text{C}_n\text{H}_{2n} + n\text{H}_2\text{O}$.
10. If a reactant is either very strongly or weakly adsorbed on a catalytic surface, the catalytic activity will be small. This is because if the adsorption is strong the chemisorptive bond is strong to break, while if it is weak the surface coverage is small.

Section 2. Short answers

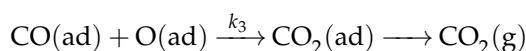
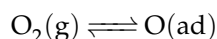
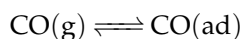
1. The first order reaction $\text{A}(\text{g}) \longrightarrow \text{A}(\text{ads}) \longrightarrow \text{B}(\text{g})$ has a rate of $1.8 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$ on a surface with dimensions 1.00 cm by 3.50 cm. How would the rate of the reaction change if the dimensions of the two sides of the surface were each doubled? How do you reconcile your conclusion with the interest in nanoscale materials for catalytic purposes?

Answer: Rate is increased four times implying that increasing the size would increase the rate. This appears counter to the nano revolution. But that is only a paradox. The surface area/volume ratio goes as $1/r$, which for nanosize materials is very high.

Consider the reaction $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g})$ on a surface of platinum. It is known that on this surface, O_2 adsorbs dissociatively, while CO adsorbs molecularly.

2. Write a Langmuir-Hinshelwood (LH) mechanism for this reaction. Obtain the rate law if the adsorption steps are instantaneously at equilibrium.

Answer:



The question says that the adsorption steps are instantaneously at equilibrium, which implies that the last step is the RDS.

$$v = k_3 \theta_{\text{CO}} \theta_{\text{O}}$$

We know from a quiz that

$$\theta_{\text{CO}} = \frac{b_{\text{CO}} p_{\text{CO}}}{1 + b_{\text{CO}} p_{\text{CO}} + b_{\text{O}}^{1/2} p_{\text{O}}^{1/2}}$$

and similarly

$$\theta_{\text{O}} = \frac{b_{\text{O}}^{1/2} p_{\text{O}}^{1/2}}{1 + b_{\text{CO}} p_{\text{CO}} + b_{\text{O}}^{1/2} p_{\text{O}}^{1/2}}$$

so that

$$v = \frac{k_3 b_{\text{CO}} p_{\text{CO}} b_{\text{O}}^{1/2} p_{\text{O}}^{1/2}}{\left(1 + b_{\text{CO}} p_{\text{CO}} + b_{\text{O}}^{1/2} p_{\text{O}}^{1/2}\right)^2}$$

3. If the reaction proceeds via an Eley-Rideal (ER) mechanism then $v = \frac{k_3 b_{\text{CO}} b_{\text{O}_2}^{1/2} p_{\text{CO}} p_{\text{O}_2}^{1/2}}{1 + b_{\text{O}_2}^{1/2} p_{\text{O}_2}^{1/2} + b_{\text{CO}} p_{\text{CO}}}$. Plot the prediction of the two models, the rate expression that you derived in question (2) and the ER expression above, as a function of the partial pressure of CO(g) at a fixed pressure of O₂(g). (Hint: Obtain the limiting forms of the two expressions at low and high CO partial pressures.)

Answer: As suggested in the hint, let us look at the low and high p_{CO} forms of the two rate expressions. At low p_{CO} , both LH and ER show a linear dependence on p_{CO} , while at high p_{CO} , the LH has a $1/p_{\text{CO}}$ dependence and the ER is independent of p_{CO} . So the v vs. p_{CO} graphs in both cases go through the origin and are linear wrt p_{CO} at low pressures. At high pressures, the ER graph is horizontal (independent of p_{CO}), while the LH graph is a rectangular hyperbola (like the $P - V$ plot for an ideal gas).

The energy of adsorption, E_{ads} , can be measured by a technique called temperature programmed desorption (TPD). In a TPD experiment, the temperature, (T), of the surface with bound adsorbate is changed according to the equation $T = T_0 + \alpha t$, where T_0 is the initial temperature, α is a constant that determines the rate at which the temperature is changed, and t is the time. A mass spectrometer is used to measure the concentration of molecules that desorb from the surface. The analysis of TPD data depends on the kinetic model of desorption. Consider a first order desorption process $\text{M-S(s)} \xrightarrow{k_d} \text{M(g)} + \text{S(s)}$.

4. Write an expression for the rate law for desorption and then show that

$$\frac{d[\text{M-S}]}{dT} = -\frac{[\text{M-S}]}{\alpha} \left(\tau_0^{-1} e^{-E_{\text{ads}}/RT} \right).$$

Here τ_0 is the vibrational lifetime.

Answer:

$$\frac{d[\text{M-S}]}{dT} = \frac{d[\text{M-S}]}{dt} \frac{dt}{dT}$$

$$\frac{d[\text{M-S}]}{dt} = -k_d [\text{M-S}]$$

$$dT = \alpha dt$$

$$\frac{1}{k_d} = \tau = \tau_0 e^{-E_{\text{des}}/RT} = \tau_0 e^{E_{\text{ads}}/RT}$$

from which the result follows.

5. With increasing T , $\frac{d[\text{M-S}]}{dT}$ initially increases, then reaches a maximum, after which it decreases. Let $T = T_{\text{max}}$ be the temperature corresponding to the maximum rate of desorption. Show that $\frac{E_{\text{ads}}}{RT_{\text{max}}} = \frac{\tau_0^{-1}}{\alpha} e^{-E_{\text{ads}}/RT_{\text{max}}}$. Remember that $[\text{M-S}]$ is a function of temperature.

Answer: From the calculus we know that at the maximum, the first derivative is zero. In this case, this implies that $\frac{d \ln \frac{M-S}{dT}}{dT} = 0$, which yields the required result.

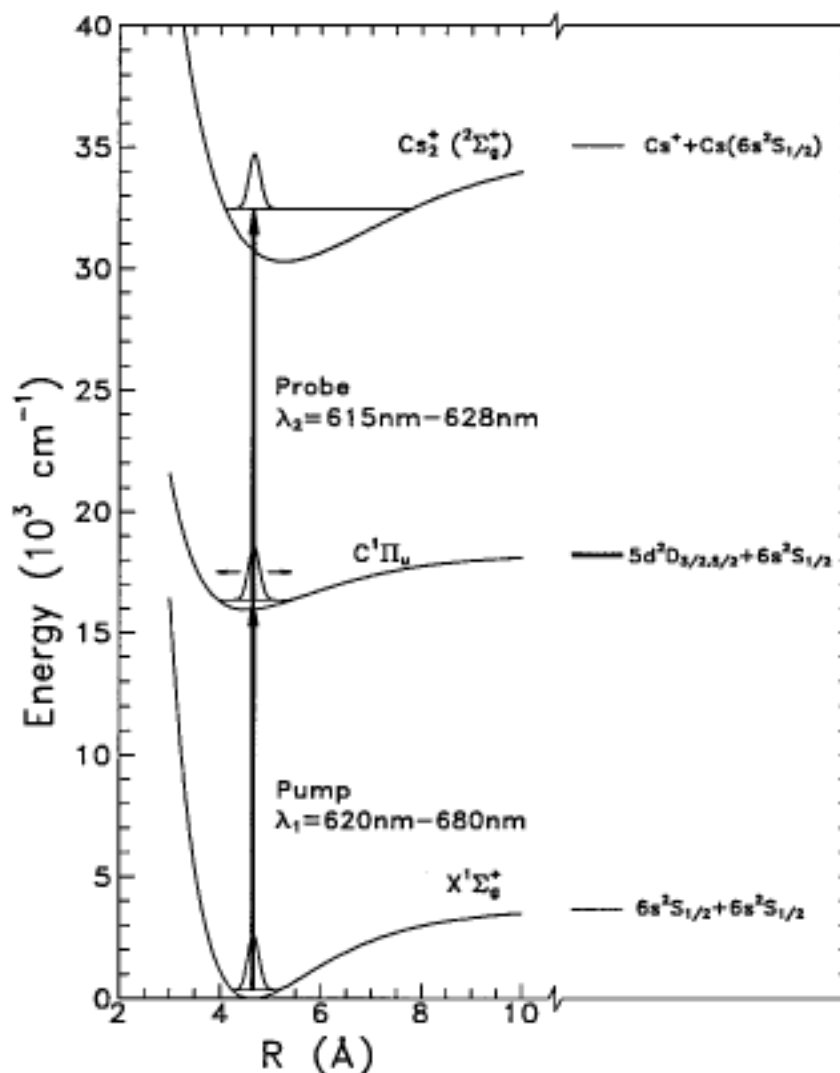
6. The equation in question 5 can be written as

$$2 \ln T_{\max} - \ln \alpha = \frac{E_{\text{ads}}}{RT_{\max}} + \ln \frac{E_{\text{ads}}}{R\tau_0^{-1}}.$$

Suggest how you would use this equation to determine τ_0 and E_{ads} .

Answer: Determine T_{\max} for different values of α and plot the LHS vs. $\frac{1}{T_{\max}}$. The slope gives E_{ads}/R and the intercept is $\ln(\text{slope}/\tau_0^{-1})$.

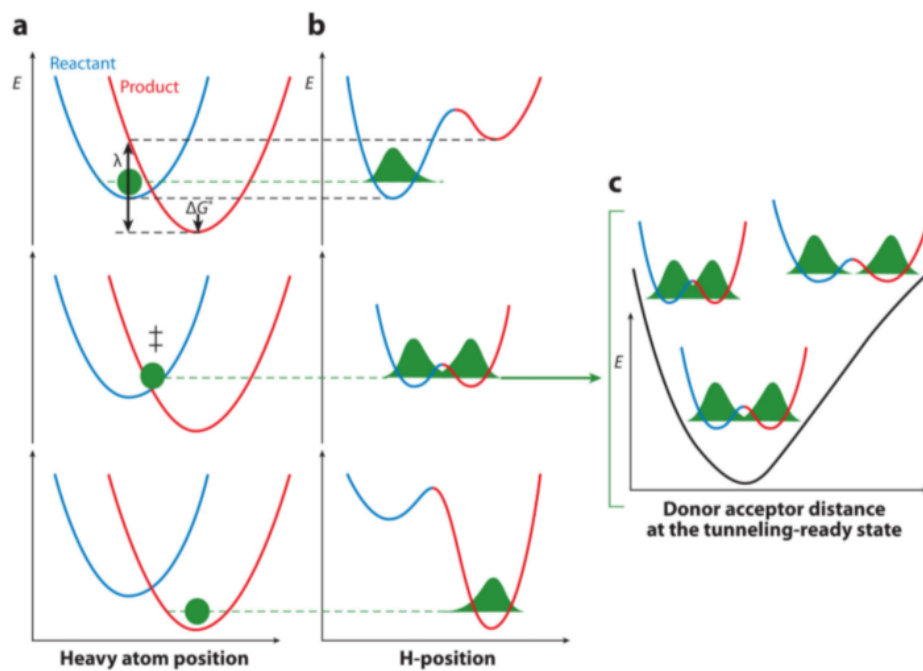
7. On heating Cs vapor a small amount of Cs_2 is formed. Absorption of light around 620–680 nm excites Cs_2 molecules from the ground $X^1\Sigma_g^+$ state to the $C^1\Pi_u$ state. The latter state is photoionized on absorbing light of 615–628 nm giving detectable signal. All the relevant states are well-represented by Morse potentials. Show the relevant states on a potential energy diagram and explain how you would conduct a femtosecond pump-probe experiment to study the dynamics of Cs_2 in the $C^1\Pi_u$ state.



Answer:

8. With the help of a series of diagrams of the potential energy surface along components of the collective reaction coordinate, show the effect of heavy-atom motions on the zero-point energy

in the reactant and product potential well for Marcus-like model of H-tunneling. Identify the reorganization energy and the driving force on the diagram.



Answer: