The pressure of O_2 gas required to give a particular coverage of adsorbed oxygen atoms on a silver surface at 427 °C was 1 mbar. However, at 527 °C, a pressure of 36 mbar was necessary to establish the same constant surface coverage.

1. *(7 points)* Estimate the isosteric enthalpy of adsorption for $O_2(g)$ on Ag.
2. *(3 points)* Is $O_2(g)$ chemisorbed or physisorbed on Ag? Why?

On a surface with dimensions 1.00 cm by 3.50 cm the first order reaction $A(g) \longrightarrow A(ads) \longrightarrow B(g)$ has a rate of $1.8 \times 10^{-4}\,mol\,dm^{-3}\,s^{-1}$.

3. *(4 points)* How would the rate of the reaction change if the dimensions of the two sides of the surface were each doubled? Why?
4. *(6 points)* How do you reconcile your conclusion with the interest in the use of nanoscale materials for catalytic purposes?

The enzyme carbonic anhydrase catalyzes the reaction $CO_2 + H_2O \longrightarrow HCO_3^- + H^+$.

5. *(4 points)* If 8.0 µg of this enzyme (molar mass $30.0\,kg\,mol^{-1}$) catalyzes the hydration of 0.146 g of CO_2 in 30 s, estimate the turnover number.
6. *(6 points)* For this enzyme, when CO_2 is present in excess the Michaelis constant and turnover number are 1.2×10^{-2} M and $1 \times 10^6\,s^{-1}$, while in the presence of excess HCO_3^- they are 2.6×10^{-2} M and $4 \times 10^5\,s^{-1}$ respectively. Determine ALL the rate constants for the elementary steps in the reaction mechanism.

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.

7. *(2 points)* The analysis of TPD data depends on the kinetic model of desorption. Consider a first order desorption process $M{-}S(s) \xrightarrow{k_d} M(g) + S(s)$. Write an expression for the rate law for desorption.
8. *(8 points)* Show that

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

where τ_0 is the vibrational lifetime.

Consider the reaction $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$ on a surface of platinum. On this surface O_2 adsorbs dissociatively and CO molecularly.

9. *(4 points)* Write a Langmuir-Hinshelwood (LH) mechanism for this reaction.
10. *(6 points)* Obtain an expression for the rate of the reaction in terms of the partial pressures of the gases if the adsorption steps are instantaneously at equilibrium.