

3.091 OCW Scholar

# **Self-Assessment**

## **Reactions and Kinetics**

### **Supplemental Exam Problems for Study**

**Problem #4**

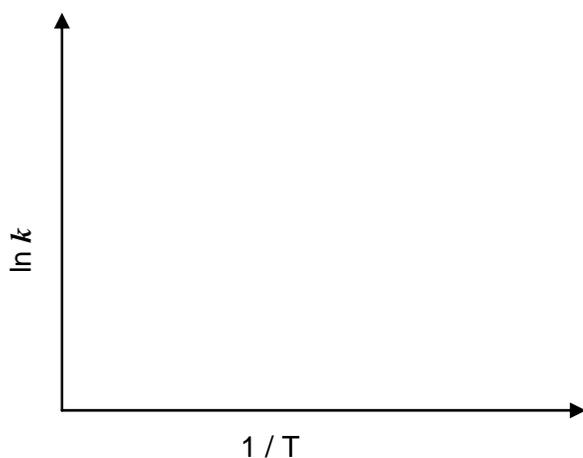
Acetaldehyde,  $\text{CH}_3\text{CHO}$ , will decompose into methane and carbon monoxide according to



At  $450^\circ\text{C}$  the rate of consumption of  $\text{CH}_3\text{CHO}$  is measured to vary with the concentration of  $\text{CH}_3\text{CHO}$  raised to the power 1.5.

- (a) With a  $\text{CH}_3\text{CHO}$  concentration of 0.222 M, the rate of consumption of  $\text{CH}_3\text{CHO}$  at  $450^\circ\text{C}$  is measured to be  $3.33 \times 10^{-3} \text{ Ms}^{-1}$ . Calculate the rate of production of carbon monoxide when the concentration of  $\text{CH}_3\text{CHO}$  has fallen to 0.111 M.

- (b) On the graph below, show how the specific chemical rate constant,  $k$ , varies with temperature when the above reaction is conducted ① in the absence of a catalyst; and ② in the presence of a catalyst. Label both lines so as to associate each with either ① or ②. The diagram is not to be drawn to scale; however, you must pay attention to relative magnitudes.



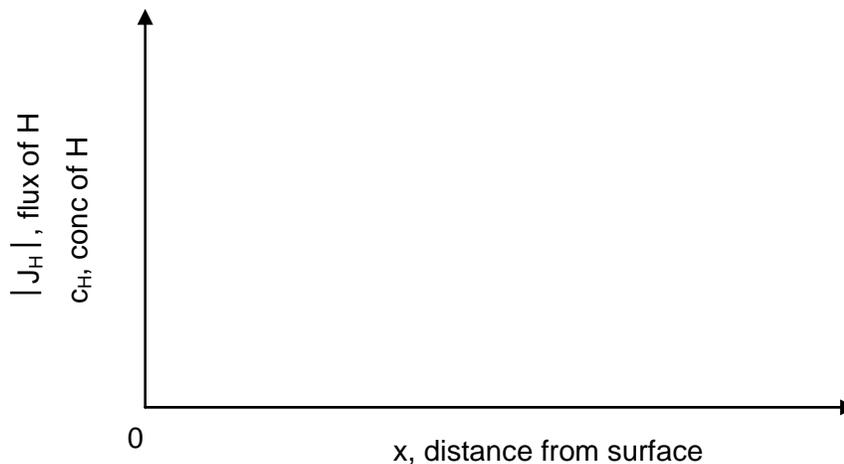
**Problem #6**

- (a) A specimen of  $\text{LaNi}_5$  containing hydrogen is placed in a vacuum furnace. After 1 hour, at what depth from the surface of the specimen has the concentration of hydrogen reached  $\frac{1}{3}$  the initial concentration? The diffusion coefficient of hydrogen in the alloy has a value of  $3.091 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . Assume that the initial concentration of hydrogen is uniform throughout the specimen and that the concentration of hydrogen is maintained at zero in the vacuum furnace.

DATA: Error Function Values (given without regard as to whether you need these data to solve the problem)

for values of  $\xi < 0.6$ , use the approximation  $\text{erf}(\xi) = \xi$ ;  $\text{erf}(1.0) = 0.843$ ;  $\text{erf}(2.0) = 0.998$

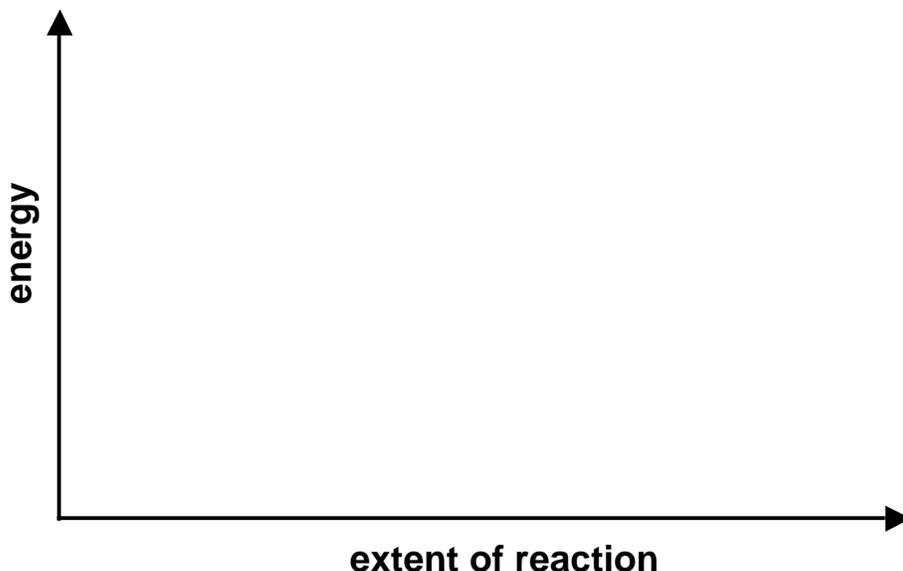
- (b) On the same graph below, sketch the profiles of ❶ the concentration of hydrogen,  $c_{\text{H}}$ , and ❷ the absolute magnitude of the flux of hydrogen,  $|J_{\text{H}}|$ , in the near-surface region of the specimen of part (a) at time,  $t_1$ , where  $0 < t_1 < 1 \text{ h}$ .



**Problem #3**

Azomethane,  $\text{CH}_3\text{N}_2\text{CH}_3$ , decomposes at 600 K to ethane,  $\text{C}_2\text{H}_6$ , and nitrogen,  $\text{N}_2$ . The reaction has been measured to be first order in azomethane.

- (a) Write the rate law expression for the decomposition of azomethane.
- (b) The value of the half-life,  $t_{1/2}$ , for this reaction has been measured to be 1920 s. How much of the initial amount of azomethane remains after 3.091 h? Express your answer as a *fraction* of the initial concentration,  $c_0$ , of azomethane.
- (c) On the plot below, sketch the variation in energy ( $\approx$ chemical potential) with extent of reaction for the decomposition of azomethane. Assume that the ratio of  $E_a/\Delta E_{\text{reaction}} = -3$ , where  $E_a$  represents the activation energy and  $\Delta E_{\text{reaction}}$  the energy change of the reaction. Label  $E_a$  and  $\Delta E_{\text{reaction}}$ . Label the energy states of  $\text{CH}_3\text{N}_2\text{CH}_3$ ,  $\text{C}_2\text{H}_6$ , and  $\text{N}_2$ .



- (d) How does a catalyst change the ratio of the absolute value of  $E_a/\Delta E_{\text{reaction}}$ ? Increase? Decrease? No change? Justify your answer by explaining what happens at the atomic level in the catalysis of a reaction in which all the reactants and products are gases.

**Problem #4**

There is a differential nitrogen pressure across a furnace wall made of steel measuring 2.22 mm in thickness. The concentration of nitrogen at the inner surface of the wall is held constant at  $9.99 \text{ kg m}^{-3}$ , while the concentration at the outer surface of the wall is held constant at  $1.11 \text{ kg m}^{-3}$ . The area of the wall is  $3.33 \text{ m}^2$ , and the diffusivity of nitrogen in steel at the furnace operating temperature is  $D_N = 3.091 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ .

- (a) What is the total rate loss of nitrogen from the furnace at steady state? Express your answer in units of  $\text{kg s}^{-1}$ .
- (b) If the steel of the wall were replaced with another steel of the identical composition but with a grain size  $10\times$  larger than that of the steel in part (a), how would the loss of nitrogen from the furnace change? Explain.

**Problem #6**

- (a) The energy of vacancy formation,  $\Delta H_v$ , in palladium (Pd) is 1.5 eV. At 888°C there is one vacancy for every million ( $10^6$ ) atom sites. Is it possible, by simply raising the temperature and ***not exceeding the melting point of the metal***, to achieve a vacancy fraction of one vacancy for every thousand ( $10^3$ ) atom sites?
- (b) You are given two specimens of Pd, each of identical purity. Specimen ❶ has a grain size of 3.091  $\mu\text{m}$ ; specimen ❷ has a grain size of 444  $\mu\text{m}$ . Which specimen will exhibit a higher rate of diffusion of hydrogen through it? Explain the reason for your choice.

**Problem #11**

Sulfuryl chloride,  $\text{SO}_2\text{Cl}_2$ , decomposes to  $\text{SO}_2$  and  $\text{Cl}_2$  according to



The reaction is first order in  $\text{SO}_2\text{Cl}_2$ , and the value of the rate constant,  $k$ , is  $2.2 \times 10^{-5} \text{ s}^{-1}$ .

- (a) Calculate the initial rate of reaction when a reactor is charged with  $\text{SO}_2\text{Cl}_2$  at a concentration of  $0.11 \text{ mol L}^{-1}$ . Express your answer in units of  $\text{mol L}^{-1} \text{ s}^{-1}$ .
- (b) Calculate how long it will take for the concentration of  $\text{SO}_2\text{Cl}_2$  in the reactor in part (a) to fall to  $\frac{1}{4}$  of its initial value. Express your answer in units of s.

**Problem #12**

(a) The diffusion coefficient of oxygen in silicon,  $D_{\text{O}}$ , has been measured to have the following values:

$D_{\text{O}}$ ( $\text{cm}^2 \text{s}^{-1}$ )	T ( $^{\circ}\text{C}$ )
$9.2 \times 10^{-11}$	1100
$1.4 \times 10^{-9}$	1300

Show that in order to increase the value of  $D_{\text{O}}$  by a factor of  $10\times$  greater than it is at  $1300^{\circ}\text{C}$  would require raising the temperature above the melting point of silicon.

(b) Make a crude estimate showing that it is feasible to remove oxygen from a silicon ribbon of thickness  $0.1 \mu\text{m}$  by exposing the ribbon to vacuum for 10 minutes at a temperature of  $1100^{\circ}\text{C}$ .

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