

# Self-Assessment Exam

## Reactions & Kinetics

**Write your answers on these pages.**

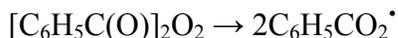
**State your assumptions and show calculations that support your conclusions.**

RESOURCES PERMITTED: PERIODIC TABLE OF THE ELEMENTS, TABLE OF CONSTANTS,  
AN AID SHEET (ONE PAGE  $8\frac{1}{2}'' \times 11''$ ), AND A CALCULATOR.

**NO BOOKS OR OTHER NOTES ALLOWED.**

### Exam 3, Problem #4

In the 1920s Jack Breitbart of Revlon Laboratories found that acne could be treated by the use of benzoyl peroxide ( $[\text{C}_6\text{H}_5\text{C}(\text{O})]_2\text{O}_2$ ). The oxygen-oxygen bond in peroxides is weak and under the influence of modest heating, benzoyl peroxide readily decomposes to form free radicals according to:

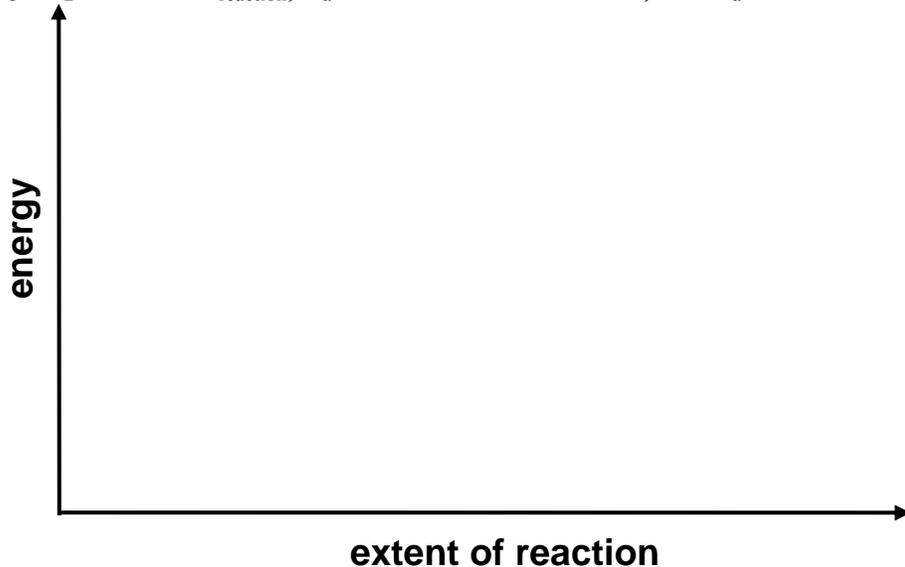


The rate of decomposition was measured at  $92^\circ\text{C}$  at various concentrations and found to be:

$c$ , concentration of $[\text{C}_6\text{H}_5\text{C}(\text{O})]_2\text{O}_2$ (M)	$r$ , rate of decomposition of $[\text{C}_6\text{H}_5\text{C}(\text{O})]_2\text{O}_2$ (M/s)
1.00	$2.22 \times 10^{-4}$
0.25	$0.56 \times 10^{-4}$

(a) Determine the order of reaction for the decomposition of benzoyl peroxide.

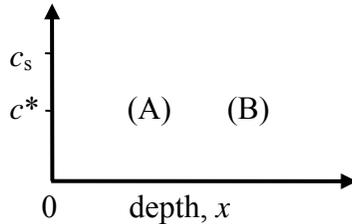
(b) On the plot below, sketch the variation in energy with extent of reaction for the decomposition of benzoyl peroxide. Assume that the ratio of  $E_a/\Delta E_{\text{reaction}} = -2.5$ , where  $E_a$  represents the activation energy and  $\Delta E_{\text{reaction}}$  the energy change of the reaction. Label the energy states of  $[\text{C}_6\text{H}_5\text{C}(\text{O})]_2\text{O}_2$  and  $\text{C}_6\text{H}_5\text{CO}_2^\cdot$ . Label  $\Delta E_{\text{reaction}}$ ,  $E_a$  for the forward reaction, and  $E_a$  for the back reaction.



(c) On the same plot above, sketch the variation in energy with extent of reaction for the decomposition of benzoyl peroxide under the influence of a catalyst.

### Exam 3, Problem #5

- (a) Specimens of steel are being surface hardened by the introduction of carbon. The concentration of carbon at the free surface of the steel is kept constant at  $c_s$ . Chemical analysis of a number of specimens indicates that after time,  $t_1$ , the carbon concentration has a value of  $c^*$  at a depth from the surface,  $x_1$ , shown below at (A), and that after time  $t_2 = 2t_1$ , the carbon concentration has a value of  $c^*$  at a depth  $x_2 = 2x_1$ , shown below at (B). Under these conditions, would you describe the rate of carburization as (1) steady state diffusion; (2) transient state diffusion; or (3) not governed by diffusion, i.e., rate limited by some other process. Justify your choice.



- (b) If the steel specimens in part (a) were replaced with steel specimens of identical composition but with a dislocation density  $10\times$  greater than that of the steel in part (a), how would the rate of uptake of carbon change? Explain.

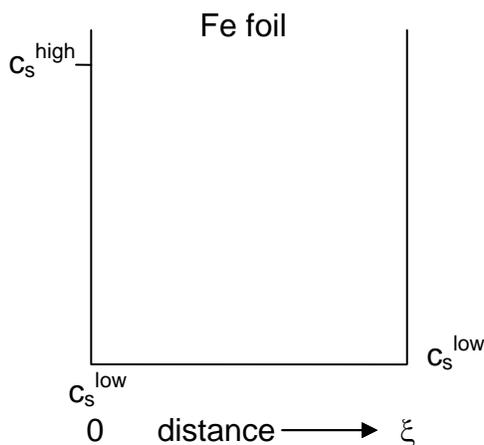
## Final Exam, Problem #1

- (a) A membrane is to be manufactured to the following specifications. At 700°C the leak rate of hydrogen at steady state is not to exceed  $10^{-3} \text{ mol cm}^{-2} \text{ hr}^{-1}$  when the concentrations of hydrogen are maintained at  $c_s^{\text{high}} = 7.7 \times 10^{19} \text{ atoms cm}^{-3}$  on one side of the membrane and  $c_s^{\text{low}} =$  effectively zero on the other side. What is the minimum thickness,  $\xi$ , of iron foil that will meet these requirements? The diffusion coefficient of atomic hydrogen in iron,  $D_{\text{H}}$ , at 700°C is  $3.091 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ . Express your answer in units of cm.

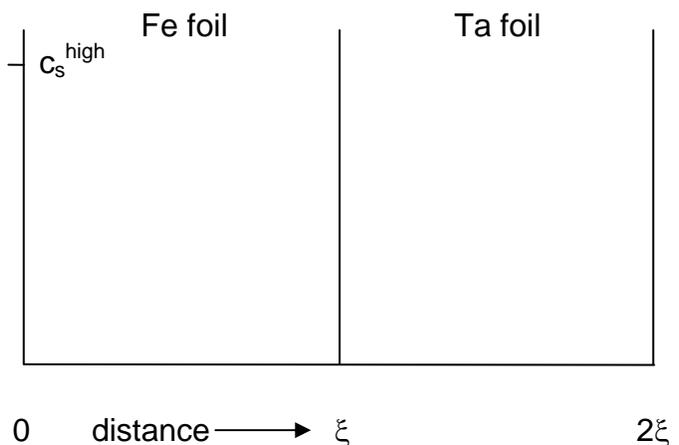
- (b) Sketch in Figure 1 the steady-state concentration profile in the membrane under the conditions described in part (a).

- (c) Assume now that the membrane consists of two layers, one made of iron foil identical to that specified in part (a) and one made of tantalum foil. The layers are identical in thickness. The value of  $D_{\text{H}}$  in iron ( $D_{\text{H}}^{\text{Fe}}$ ) is 5× the value of  $D_{\text{H}}$  in tantalum ( $D_{\text{H}}^{\text{Ta}}$ ). Under identical conditions to those described in part (a), sketch in Figure 2 the steady-state concentration profile in the bilayer membrane. Just estimate the shape of the trace; you need not calculate accurate values of concentration.

**Figure 1**

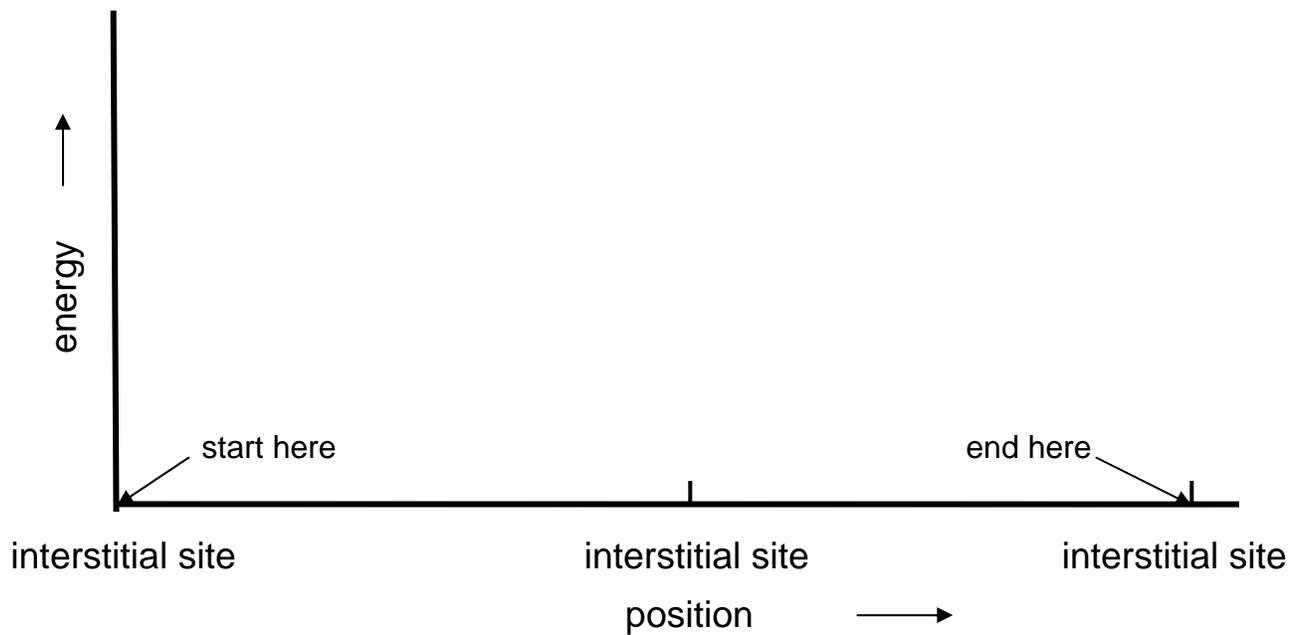


**Figure 2**



### Final Exam, Problem #3

- (a) Sketch the variation in energy with position as an impurity atom migrates through two interstitial sites.



### Final Exam, Problem #11

- (a) A first-order chemical reaction causes the concentration of a reagent to fall by a factor of 11 over a period of 11 minutes. Determine the half-life of the reaction. Express your answer in units of minutes.

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