3.091 OCW Scholar

# Self-Asessment

# Reactions and Kinetics

# Supplemental Exam Problems for Study

## Solutions Key

## Problem #4

Acetaldehyde, $CH_3CHO$, will decompose into methane and carbon monoxide according to

$$CH_3CHO\ (g) \Rightarrow CH_4\ (g) + CO\ (g)$$

At 450ºC the rate of consumption of $CH_3CHO$ is measured to vary with the concentration of $CH_3CHO$ raised to the power 1.5.

(a) With a $CH_3CHO$ concentration of 0.222 M, the rate of consumption of $CH_3CHO$ at 450ºC is measured to be $3.33 \times 10^{-3}\ Ms^{-1}$. Calculate the rate of production of carbon monoxide when the concentration of $CH_3CHO$ has fallen to 0.111 M.

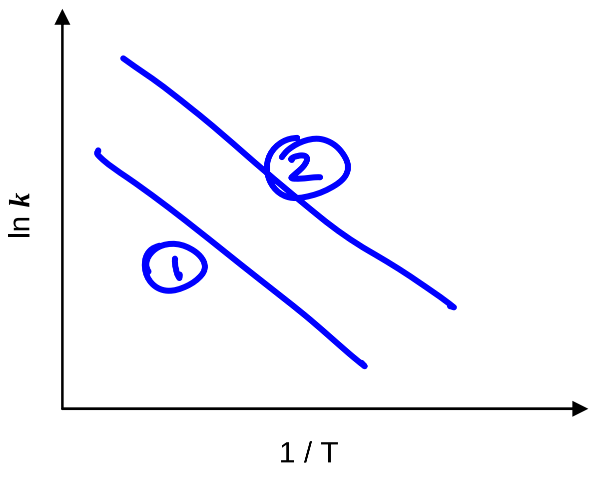
let $c = [CH_3CHO]$

$$\therefore -\frac{dc}{dt} = kc^{1.5} \Rightarrow k = \frac{-dc/dt}{c^{1.5}} = \frac{3.33\times10^{-3}}{(0.222)^{1.5}}$$

by stoichiometry, rate of prod$^n$ of $CO_2$ = rate of consumption of $CH_3CHO$

$$\therefore \frac{dc}{dt} = kc^{1.5} = \frac{3.33\times10^{-3}}{(0.222)^{1.5}} \cdot (0.111)^{1.5} = 1.18\times10^{-3}\ Ms^{-1}$$

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



## Problem #6

(a) A specimen of $LaNi_5$ 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 ⅓ the initial concentration? The diffusion coefficient of hydrogen in the alloy has a value of $3.091 \times 10^{-6}$ $cm^2$ $s^{-1}$. 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)

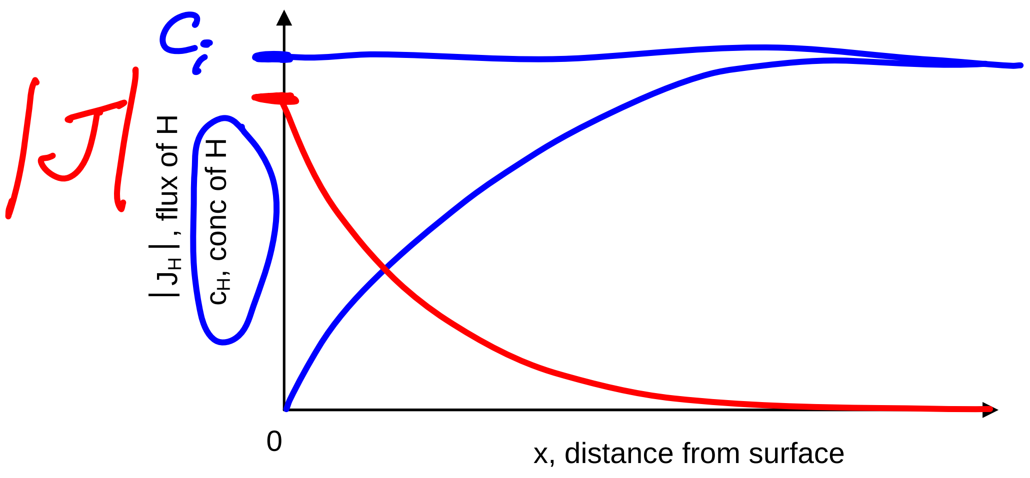
for values of $\xi < 0.6$, use the approximation $erf(\xi) = \xi$; $erf(1.0) = 0.843$; $erf(2.0) = 0.998$

$$\frac{c-c_s}{c_i-c_s} = erf\frac{x}{2\sqrt{Dt}} = \frac{\frac{1}{3}c_s - c_s}{0-c_s} = \frac{\frac{1}{3}-1}{-1} = \frac{2}{3}$$

chose $erf\frac{x}{2\sqrt{Dt}} = 0.67 \Rightarrow \frac{x}{2\sqrt{Dt}} = 0.67$

$$\therefore \; x = 0.67 \times 2 \times \sqrt{Dt}$$
$$= 0.67 \times 2 \times (3.091 \times 10^{-6} \times 3600)^{1/2}$$
$$= 0.141 \text{ cm}$$

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



## Problem #3

Azomethane, $CH_3N_2CH_3$, decomposes at 600 K to ethane, $C_2H_6$, and nitrogen, $N_2$. The reaction has been measured to be first order in azomethane.

(a) Write the rate law expression for the decomposition of azomethane.

$$-\frac{dc}{dt} = kc \quad \text{where} \quad c = [CH_3N_2CH_3]$$

(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, $c_o$, of azomethane.

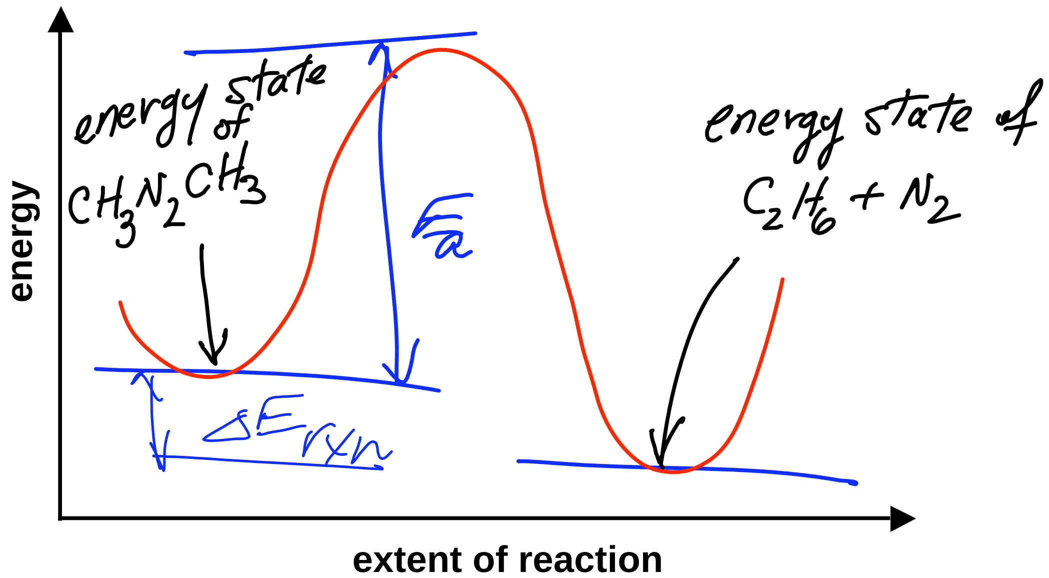
$\ln c/c_o = -kt$ for 1st order rxns & $k = 0.693/t_{1/2}$

$$\therefore c/c_o = \exp -\frac{0.693}{t_{1/2}} t = \exp -\frac{0.693 \times 3.091 \times 3600}{1920} = 1.80 \times 10^{-2}$$

or $3.091\ h = (3.091 \times 3600)/1920 = 5.8$ half lives

$$\Rightarrow c/c_o = \left(\frac{1}{2}\right)^{5.8} = 1.79 \times 10^{-2}$$

(c) On the plot below, sketch the variation in energy (≈chemical potential) with extent of reaction for the decomposition of azomethane. Assume that the ratio of $E_a/\Delta E_{reaction} = -3$, where $E_a$ represents the activation energy and $\Delta E_{reaction}$ the energy change of the reaction. Label $E_a$ and $\Delta E_{reaction}$. Label the energy states of $CH_3N_2CH_3$, $C_2H_6$, and $N_2$.



(d) How does a catalyst change the ratio of the absolute value of $E_a/\Delta E_{reaction}$? 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.

decrease. catalyst reduces the activation barrier. at the atomistic level, the catalyst adsorbs $CH_3N_2CH_3$ and facilitates breaking the N=N double bond

## 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 kg $m^{-3}$, while the concentration at the outer surface of the wall is held constant at 1.11 kg $m^{-3}$. The area of the wall is 3.33 $m^2$, and the diffusivity of nitrogen in steel at the furnace operating temperature is $D_N = 3.091 \times 10^{-10}$ $m^2$ $s^{-1}$.

(a) What is the total rate loss of nitrogen from the furnace at steady state? Express your answer in units of kg $s^{-1}$.

$$\frac{dm}{dt} = JA = \left(-D\frac{dc}{dx}\right)A = -DA\frac{\Delta c}{\Delta x}$$

now neglect minus sign

$$= 3.091\times10^{-10}\times3.33\times\frac{(9.99-1.11)}{2.22\times10^{-3}} = 4.12\times10^{-6}\ \text{kg/s}$$

(b) If the steel of the wall were replaced with another steel of the identical composition but with a grain size 10× larger than that of the steel in part (a), how would the loss of nitrogen from the furnace change? Explain.

as grain size increases, The ratio of grain bdry to bulk <u>DECREASES</u>. Since $D_{bulk} < D_{gb}$,

expect $\frac{dm}{dt}$ to decrease

## 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?

$$f_V = A \exp - \frac{\Delta H_v}{k_B T}$$

at 888°C, $f_V = 10^{-6}$

we want T at which $f_V = 10^{-3}$

$$\therefore \frac{f_V}{A} = \exp - \frac{\Delta H_v}{k_B T}$$

$$\therefore \ln \frac{f_V}{A} = - \frac{\Delta H}{kT}$$

$$\therefore T = - \frac{\Delta H}{k} \left\{ \ln \frac{f_V}{A} \right\}^{-1}$$

get value of A using data at 888°C = 1161 K

$$A = f_V \Big/ \exp - \frac{\Delta H}{kT}$$

convert to 1161 K

$$\therefore T = - \frac{1.5 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23}} \left\{ \ln \frac{10^{-3}}{\dfrac{10^{-6}}{\exp - \dfrac{1.5 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times 1161}}} \right\}^{-1}$$

Convert eV to J

$= 2155$ K

$= 1882$ °C > m.p. Pd

Answer: NO!

(b) You are given two specimens of Pd, each of identical purity. Specimen ❶ has a grain size of 3.091 µm; specimen ❷ has a grain size of 444 µm. Which specimen will exhibit a higher rate of diffusion of hydrogen through it? Explain the reason for your choice.

The diffusivity of hydrogen will be orders of magnitude higher along the grain boundaries of Pd than through the bulk of the crystal. Hence, the specimen with more grain boundary per unit volum will exhibit a higher rate of hydrogen permeation. Assuming that the width of the grain boundary is invariant with grain size, specimen ❶ will have more grain boundary per unit volume and therefore a higher rate of hydrogen permeation.

## Problem #10 (7 points)

Sulfuryl chloride, $SO_2Cl_2$, decomposes to $SO_2$ and $Cl_2$ according to

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g).$$

The reaction is first order in $SO_2Cl_2$, and the value of the rate constant, $k$, is $2.2 \times 10^{-5}\ s^{-1}$.

(a) Calculate the initial rate of reaction when a reactor is charged with $SO_2Cl_2$ at a concentration of 0.11 mol $L^{-1}$. Express your answer in units of mol $L^{-1}\ s^{-1}$.

3 $$\frac{dc}{dt} = -kc = 2.2\times10^{-} \times 0.11 = 2.42\times10^{-}$$

(b) Calculate how long it will take for the concentration of $SO_2Cl_2$ in the reactor in part (a) to fall to ¼ of its initial value. Express your answer in units of s.

4 method 1 : calculate $t_{1/2} = \frac{\ln 2}{k}$ & use

$\frac{1}{4} = \left(\frac{1}{2}\right)^2 \Rightarrow$ 2 half lives $= 6.30\times10^4$ s

method 2 : $\ln C_o/C = kt$ & set $C = \frac{1}{4} C_o$

$$\Rightarrow t_{1/4} = \frac{\ln 4}{k} = 6.30\times10^4\ s$$

## Problem #12

(a) The diffusion coefficient of oxygen in silicon, $D_O$, has been measured to have the following values:

| $D_O$ (cm$^2$ s$^{-1}$) | T (°C) |
|---|---|
| $9.2 \times 10^{-11}$ | 1100 |
| $1.4 \times 10^{-9}$ | 1300 |

Show that in order to increase the value of $D_O$ by a factor of 10× greater than it is at 1300°C would require raising the temperature above the melting point of silicon.

$D = D_0 \exp -\frac{Q}{RT} \Rightarrow$ find $T'$ at which $D = 10 \times D_{1300}$

need to get the value of $Q$ // $\frac{D_{1300}}{D_{1100}} = \frac{\exp -\frac{Q}{R1573}}{\exp -\frac{Q}{R1373}} = \frac{1.4\times10^{-9}}{9.2\times10^{-11}} = 15.22$

$\Rightarrow \exp\frac{-Q}{1573R} = 15.22 \exp -\frac{Q}{1373R}$

$\therefore \frac{-Q}{1573R} = \ln 15.22 - \frac{Q}{1373R}$

$\therefore Q = R \ln 15.22 \left(\frac{1}{1373} - \frac{1}{1573}\right)^{-1}$

$= 244 \times 10^3$ J/mol

now solve for $T'$ $\Longrightarrow$

$\exp -\frac{Q}{RT} = 10 \exp \frac{-Q}{R1573}$

$\therefore \frac{-Q}{RT} = \ln 10 - \frac{Q}{R1573}$

$\therefore T = \frac{-Q}{R\left(\ln 10 - \frac{Q}{1573R}\right)}$

$\therefore T = \frac{-244000}{8.314\left(\ln 10 - \frac{244000}{1573 \times 8.314}\right)} = 1794\text{ K} = 1521°\text{C} >$ mp Si

(b) Make a crude estimate showing that it is feasible to remove oxygen from a silicon ribbon of thickness 0.1 μm by exposing the ribbon to vacuum for 10 minutes at a temperature of 1100°C.

$x^2 \approx Dt = 9.2\times10^{-11} \times 10 \times 60 = 5.52\times10^{-8}\text{ cm}^2$

$\therefore x = 2.35\times10^{-4}\text{ cm} = 2.35\ \mu\text{m} \gg 0.1\ \mu\text{m}$

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