

CHEM 360 PROBLEM SET 8

1. Estimate the pressure required to boil CS₂ at 25°C in a vacuum distillation. The normal boiling point is 46.25°C and the enthalpy of vaporization is 28.1 kJ mol⁻¹).

$$\ln \frac{P}{P^\circ} = -\frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_b} \right)$$

P° = 1 bar
considering normal
boiling point

$$= -\frac{\Delta H}{R} \left(\frac{1}{298.15} - \frac{1}{342.15} \right)$$

$$= -0.754$$

$$P = \underline{\underline{0.470 \text{ bar}}}$$

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2. Under certain conditions the gas phase reaction of chlorine with methane



- (a) Suppose the concentration of CH_4 is doubled. How does that change the rate of consumption of Cl_2 ? How does the rate of production of HCl change?

Since the rates are both proportional to $[\text{CH}_4]$ they will both double.

- (b) Which will have a greater effect on the rate of reaction, doubling the CH_4 concentration or doubling the Cl_2 concentration?

Doubling $[\text{Cl}_2]$ would result in a rate increase by $\sqrt{2}$,
so doubling $[\text{CH}_4]$ would have a greater effect (factor 2).

- (c) Suppose the pressure of the reaction mixture is cut in half. How would that affect the rate of reaction?

All concentrations would fall to half their original values.

The rate of reaction would thus fall by $2\sqrt{2}$.

In general:

$$\text{rate}_2/\text{rate}_1 = ([\text{CH}_4]_2/[\text{CH}_4]_1) * ([\text{Cl}_2]_2/[\text{Cl}_2]_1)^{0.5}$$

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3. The reaction rate of the gas-phase reaction $2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$ was measured for several different initial pressures of the reactants. Determine the rate equation and thence the rate constant.

$[\text{H}_2] / \text{mM}$	$[\text{NO}] / \text{mM}$	$d[\text{N}_2]/dt / \text{M s}^{-1}$	= rate
26	20	6.17×10^{-5}	
26	10.1	1.57×10^{-5}	
19	26	7.59×10^{-5}	
28.5	26	1.14×10^{-4}	

Doubling $[\text{NO}]$ with $[\text{H}_2]$ constant increases the rate by 4, so the order of NO is 2.

Increasing $[\text{H}_2]$ by 50% with $[\text{NO}]$ constant increases the rate by 50%, so the order of H_2 is 1.

The rate equation is $\frac{d[\text{N}_2]}{dt} = k[\text{H}_2][\text{NO}]^2$

the rate constant is given by $\frac{\text{rate}}{[\text{H}_2][\text{NO}]^2}$ = k

Average value for the 4 sets of data = $5.92 \text{ M}^{-2} \text{ s}^{-1}$

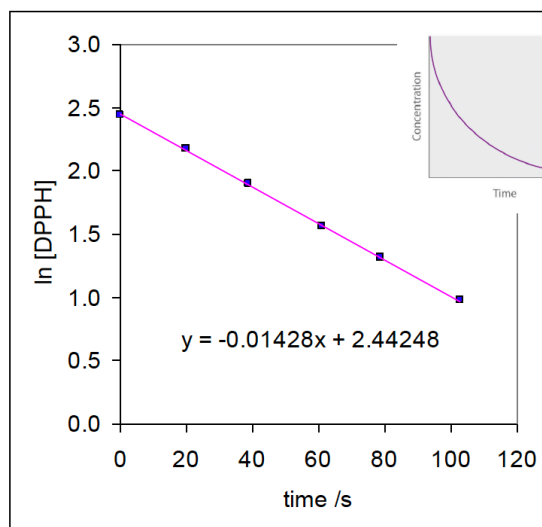
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4. The free radical DPPH reacts with Fe(II) in solution and its concentration can be followed by UV-vis spectroscopy. The rate of reaction is proportional to [Fe(II)]. For an initial concentration [Fe(II)] = 5.50×10^{-4} M, [DPPH] varies according to:

time /s	0	20	39	61	79	103
[DPPH]/ μ M	11.4	8.75	6.63	4.77	3.71	2.65

Determine the order of the reaction and the rate constant.

not necessary to use Excel!



Look at the attached plots above this box --> They both indicate first order reactions! *Note different y-axis

The straight-line plot shows that DPPH decays by **first order kinetics**.

The Fe(II) concentration is much larger, and remains approximately constant. Thus, this is a pseudo-first order reaction with $k_1 = 1.428 \times 10^{-2} \text{ s}^{-1}$.

Since the rate of reaction is proportional to [Fe(II)] the order of reaction with respect to Fe(II) is also **one**, i.e. **overall the reaction is second-order**.

Thus the rate constant is $k_2 = 26.0 \text{ M}^{-1} \text{ s}^{-1}$

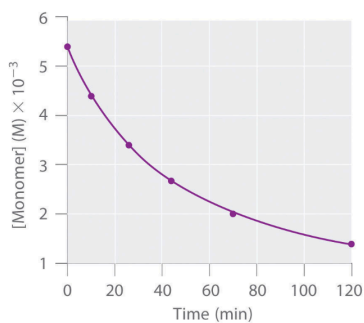
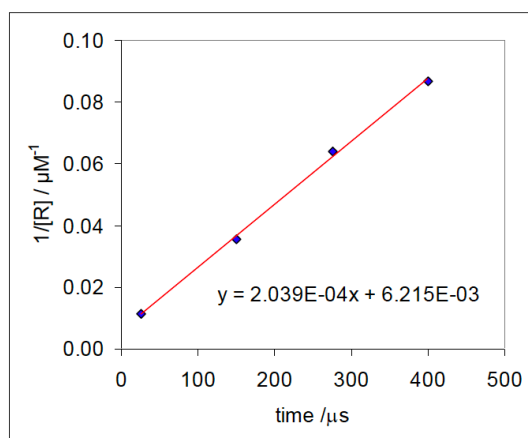
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5. The benzyl radical concentration in a pulse radiolysis experiment is found to decrease with time after the radiolysis pulse as shown in the table.

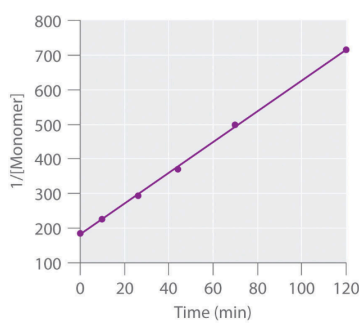
(a) Determine the order of the reaction and the relevant rate constant.

$t / \mu\text{s}$	$[\text{R}] / \mu\text{M}$	$1/[\text{R}] / \mu\text{M}^{-1}$
25	87.4	0.011
150	28.0	0.036
275	15.6	0.064
400	11.5	0.087

Look at the attached plots below this box -->
They both indicate second order reactions!
*Note different y-axis



(a)



(b)

Since a plot of $1/[R]$ against time gives a straight line, the reaction is second order.

$$\text{Slope} = 204 \text{ M}^{-1} \mu\text{s}^{-1}$$

$$\underline{2k = 2.04 \times 10^8 \text{ s}^{-1}}$$

(b) How long does it take for the benzyl radical concentration to decay to half what it is immediately following the radiolysis pulse?

$$\text{From the intercept, } 1/[R]_0 = 6215 \text{ M}^{-1}$$

$$\text{Half the initial concentration corresponds to } 2/[R]_0 = 12430 \text{ M}^{-1}$$

$$\text{which occurs at } (12430 - 6215)/204 = \underline{30.5 \mu\text{s}}$$