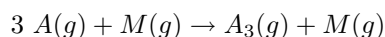


CHEM 3410: Physical Chemistry I — Fall 2008

More kinetics practice problems

December 1, 2008

1. For the following recombination reaction:



the empirical rate law is believed to have the form:

$$\frac{d[A_3]}{dt} = k[M]^\alpha [A_2]^\beta [A]^\gamma$$

where α , β , and γ are the orders with respect to A, A_2 and A, which are to be determined by initial rate data. [NOTE that A_2 is not a typo. The species A_2 is found empirically to be involved in the reaction mechanism.]

- (a) The rate of the reaction can be monitored by observing either $\frac{d[A]}{dt}$ or $\frac{d[A_3]}{dt}$. What is the relationship between $\frac{d[A]}{dt}$ and $\frac{d[A_3]}{dt}$ imposed by the reaction stoichiometry?
- (b) The observed initial rates obtained from measurements of $[A]$ at some early time and the initial amount of A are (concentrations in molarity, M):

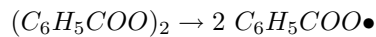
Table 1: default

[A]	[A_2]	[M]	rate
0.01	0.01	1.00	1.0
0.02	0.01	1.00	4.0
0.02	0.02	1.00	8.0
0.02	0.01	0.50	2.0

What are the values of α , β , γ , and k ?

2. On November 23, 2006 former KGB agent Aleksander Litvinenko died after receiving a lethal dose of ^{210}Po (polonium-210). ^{210}Po is produced by neutron irradiation of bismuth in a high-flux nuclear reactor. ^{210}Po decays by emitting one α -particle. The half-life for ^{210}Po is 138 days.
- (a) What is the radioactive decay rate constant of ^{210}Po ? Express your results in units of sec^{-1} . Radioactive decay follows first order kinetics.
- (b) If Mr. Litvinenko ingested $2.1 \mu\text{g}$ ($2.1 \times 10^{-6} \text{ g}$) of ^{210}Po , how many radioactive disintegrations per second occurred in his body immediately after he was poisoned?
- (c) Mr. Litvinenko survived for twenty days after he was poisoned with ^{210}Po . What was the total number of α -particles emitted inside his body as a result of radioactive disintegration of the ^{210}Po ?
- (d) The human body contains 100 trillion cells ($1 \text{ trillion} = 10^{12}$). On average, how many α -particles were emitted for each one of his tissue cells?
- (e) Traces of ^{210}Po have been found at several locations in London and on BA aircraft that had recently flown the Moscow-London route. What is the mass of ^{210}Po that would have to be present in a fingerprint or other residue in order for the α -particles from the ^{210}Po to be detectable above a typical background radiation level of 2 α -particles per second? Express your answer in terms of the mass of ^{210}Po in the forensic sample.

3. The initiator in the polymerization of ethylene commonly is benzoyl peroxide, $(C_6H_5COO)_2$:



This is a first order reaction. The half-life at $100^\circ C$ is 19.8 min.

- Calculate the rate constant in min^{-1} of the reaction.
 - If the half-life is 7.30 hours, or 438 minutes, at $70^\circ C$, what is the activation energy (in kJ/mol) for the decomposition of benzoyl peroxide.
 - What conditions for the initiation reaction would favor the growth of long high molar-mass polyethylene chains?
4. Many reactions double their rate for every $10^\circ C$ rise in temperature. Assume that such a reaction takes place at 305 K and 315 K. What must its activation energy be for this statement to hold?