

CHEM 344 FALL 09 PROBLEM SET 1

Due : Friday Sept 4 2009 @ 2pm before class!

HW TO BE HANDED IN

Engel Chapter 25 : 2,10,15,21, 27,36

Tinoco Chapter 7 : 5(a-d),8,9,19 (copies attached)

EXTRA-DO NOT HAND IN , practice for exams

Engle Chapter 25 : 4,7,8,13,24

Tinoco Chapter 7 : 39 (copies attached)

More stuff next page . . .

HW TO BE HANDED IN

5. The stoichiometric equation for a reaction is



The initial rate of formation of C is measured with the following results:

Initial concentration of A (M)	Initial concentration of B (M)	Initial rate ($M s^{-1}$)
1.0	1.0	1.0×10^{-3}
2.0	1.0	4.0×10^{-3}
1.0	2.0	1.0×10^{-3}

- (a) What is the order of the reaction with respect to A?
(b) What is the order of the reaction with respect to B?
(c) Use your conclusions in parts (a) and (b) to write a differential equation for the appearance of C.
(d) What is the rate constant k for the reaction? Do not omit the units of k .

8. The following data were obtained for the concentration vs. time for a certain chemical reaction. Values were measured at 1.00 s intervals, beginning at 0.00 and ending at 20.00 s. Concentrations in mM are:

10.00, 6.91, 4.98, 4.32, 3.55, 3.21, 2.61

2.50, 2.22, 1.91, 1.80, 1.65, 1.52, 1.36

1.42, 1.23, 1.20, 1.13, 1.09, 1.00, 0.92

- (a) Plot concentration (c) vs. time, $\ln c$ vs. time, and $1/c$ vs. time.
(b) Decide whether the data best fit zero-order, first-order, or second-order kinetics. Calculate the rate constant (with units) for the reaction and write the simplest mechanism you can for the reaction.
(c) Describe an experimental method which you think might be used to measure the concentrations that are changing so rapidly. The reaction is nearly over in 20 s.

9. The kinetics of double-strand formation for a DNA oligonucleotide containing a G · T base pair was measured by temperature-jump kinetics. The reaction is:



The following data were obtained:

Temperature (°C)	k_1 ($10^5 \text{ M}^{-1} \text{ s}^{-1}$)	k_{-1} (s^{-1})
31.8	0.8	1.00
36.8	2.3	3.20
41.8	3.5	15.4
46.7	6.0	87.0

- (a) Determine E_a , ΔH^\ddagger , and ΔS^\ddagger for the forward and reverse reactions; assume that the values are independent of temperature.
- (b) Determine the standard enthalpy ΔH^0 and standard entropy ΔS^0 changes for the reaction (assumed independent of temperature) and calculate the equilibrium constant for duplex formation at 37°C.
- (c) Discuss qualitatively what you would expect to happen to ΔH^\ddagger and the standard enthalpy change for the reaction if the duplex contained one more Watson-Crick base pair. Would each increase, decrease, or remain the same?

19. The gas-phase decomposition of di-*tert*-butyl peroxide, $(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_3$, is first order in the temperature range 110°C to 280°C, with a first-order rate constant $k = 3.2 \times 10^{16} \exp[-(164 \text{ kJ mol}^{-1})/RT] \text{ s}^{-1}$.

- (a) What are the values of ΔH^\ddagger and ΔS^\ddagger for this reaction at 110°C?
- (b) Give a brief interpretation of the value of ΔS^\ddagger .
- (c) At what temperature will the reaction occur ten times faster than at 110°C?

EXTRA-DO NOT HAND IN

39. In view of the current shortage of fossil fuels (chiefly petroleum and natural gas), alternative sources of energy are being sought. An imaginative proposal is to use rubber (latex), which is a plant hydrocarbon, polyisoprene. Latex represents about 50% of the carbon fixed in photosynthesis by rubber trees! Presumably this material could be cracked and processed in refineries in a fashion analogous to that used for petroleum. Under good conditions, a rubber tree in Brazil can produce 10 kg of usable latex per year, growing at a density of about 100 trees per acre. The heat of combustion (fuel value) of hydrocarbons is about 644 kJ mol^{-1} of CH_2 , or about $46,000 \text{ kJ kg}^{-1}$.

(a) What fraction of a year's solar energy is stored in rubber crop if the incident solar energy is $4 \text{ kJ min}^{-1} \text{ ft}^{-2}$ and the Sun is shining 500 min day^{-1} , on the average? (1 acre = $43,560 \text{ ft}^2$.) [Compare your answer with the value $(\text{energy stored})/(\text{solar energy}) = 0.3$ that can be obtained from photosynthesis in the laboratory under optimal conditions.]

(b) In 2000 the total fossil fuel consumption in the United States was $14 \times 10^{16} \text{ kJ yr}^{-1}$. What fraction of the area of the United States ($3,000,000 \text{ mi}^2$) would have to be devoted to growing rubber trees (if they would grow in the climate of the United States, which they will not) to replace our present sources of fossil fuel by latex? (1 $\text{mi}^2 = 640 \text{ acres}$.)

(c) In laboratory experiments, it is found that photosynthesis occurs optimally with about 3% CO_2 in the (artificial) atmosphere. CO_2 occurs at only 0.03% in the natural atmosphere. Propose a scheme for increasing the energy yield of agricultural crops (not necessarily rubber trees) based on this observation. List some possible additional advantages and disadvantages of your scheme, based on your background in kinetics and thermodynamics.