MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Chemistry 5.68J **Chemical Kinetics** Spring Term 2003
Chem. Eng. 10.652J **Kinetics of Chemical Reactions**

Problem Set #2 Due: February 25, 2003

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1. CKD Problem 2.4

2. CKD Problem 2.6

3. CKD Problem 2.9

4. CKD Problem 2.15

5. Some complex reactions involving the oxides of nitrogen, with their empirical rate laws, are:

overall reaction	empirical rate law
1) $2N_2O_5 \rightarrow 4NO_2 + O_2$	$R_1 = k_1[N_2O_5]$
2) $NO + N_2O_5 \rightarrow 3NO_2$	$R_2 = k_2[N_2O_5][NO]/\{[NO_2] + \alpha[NO]\}$
3) $2NO_2 + O_3 \rightarrow N_2O_5 + O_2$	$R_3 = k_3[NO_2][O_3]$
4) $2O_3 + N_2O_5 \rightarrow 3O_2 + N_2O_5$	$R_4 = k_4[N_2O_5]^{2/3}[O_3]^{2/3}$

Mechanisms for reactions (1) – (4) can be constructed from the following elementary reactions:

$$N_2O_5 \underset{(b)}{\overset{(a)}{\rightleftarrows}} NO_2 + NO_3$$

$NO_2 + NO_3 \rightarrow NO_2 + NO + O_2$ (c)

$NO + NO_3 \rightarrow 2NO_2$ (d)

$NO_2 + O_3 \rightarrow NO_3 + O_2$ (e)

$2NO_3 \rightarrow 2NO_2 + O_2$ (f)

$NO + O_3 \rightarrow NO_2 + O_2$ (g)

Problem 5, continued:

(a) What are the minimum sets of elementary reactions (a) – (g) that are required to account for the observed products and rate laws for each of reactions (1) through (4)?

Example: Consider reaction "0", $NO + O_3 \rightarrow NO_2 + O_2$, with the rate law

$$R_0 = k_0 [O_3]\{[NO] + \beta[NO_2]\}.$$

Reaction "0" can be obtained by adding together

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (g)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (e)$$

$$NO + NO_3 \rightarrow 2NO_2 \quad (d)$$

The rate law is found to be

$$R_0 = -d[NO]/dt = k_g[O_3] \{[NO] + (k_e/k_g)[NO_2]\}$$

Therefore the correct answer for Reaction "0" is | d, e, g | .

(b) Find k_4 in terms of the rate constants for the elementary reactions which are included in the mechanism you found in part (a).

6. **5.68J/10.652J Spring 2003 Problem Set 2 Problem # 6: Solving Kinetic Equations Numerically Using CHEMKIN**

The Sample Transient Calculation shipped with CHEMKIN is the for the spontaneous adiabatic combustion of a stoichiometric H_2/air mixture, which according to their model takes less than a millisecond. A different H_2/air kinetic model is given in GRI-Mech 3.0. Compare the ignition times computed using the two models, then use the GRI-Mech 3.0 model to compute the time it would take a mixture of 0.3 moles CH_4, 1 mole of O_2 and 3.76 moles of N_2 to spontaneously combust. In addition to plotting the temperature, plot the major species and the transient H_2O_2 and CH_2O concentrations. You may find the plots of H, O, and OH quite interesting: why would radical concentrations drop while the temperature stays high? Turn in your four favorite plots from the set with captions that explain what you think the figures are showing, and a short commentary about the similarities and differences between H_2 and CH_4 combustion that you can infer. Also comment on the similarities or differences between the two H_2/air simulations.

All the files you need for the Sample Transient calculation of H_2/O_2 are included with CHEMKIN. You may need to copy two GRI-Mech files into your directory.

GRI-Mech Web Site at Berkeley: http://www.me.berkeley.edu/gri_mech.