CYL565 2014-15 Homework # 3

30/01/2015

Due on: 05/02/2015

All the questions in this homework are from Chapter 27 of McQuarrie and Simon's "Physical Chemistry" book. There are numerous other problems of similar nature in this book which you could solve for practice.

1. The rate law for the reaction

$$2\,H_2(g) + 2\,NO(g) \xrightarrow{k_{obs}} N_2(g) + 2\,H_2O(g)$$

is

$$\frac{d[N_2]}{dt} = k_{obs}[H_2][NO]^2.$$

Below is a proposed mechanism for this reaction

$$H_2(g) + NO(g) + NO(g) \xrightarrow{k_1} N_2O(g) + H_2O(g)$$

$$H_2(g) + N_2O(g) \xrightarrow{k_2} N_2(g) + H_2O(g)$$

Under what conditions does this mechanism give the observed rate law? Express k_{obs} in terms of the rate constants for the individual steps of the mechanism.

2. An alternative mechanism for the reaction in question 1 is

$$NO(g) + NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2(g)$$

$$H_2(g) + N_2O_2(g) \xrightarrow{k_2} N_2O(g) + H_2O(g)$$

$$H_2(g) + N_2O(g) \xrightarrow{k_3} N_2(g) + H_2O(g)$$

Under what conditions does this mechanism give the observed rate law? Express k_{obs} in terms of the rate constants for the individual steps of the mechanism. Do you favour this mechanism or that given in question 1? Explain your reasoning.

3. Consider the chain reaction between $H_2(g)$ and $Cl_2(g)$, $Cl_2(g) + H_2(g) \longrightarrow 2\,HCl(g)$. The mechanism for the reaction is

$$Cl_2(g) + M(g) \xrightarrow{k_1} 2\,Cl(g) + M(g)$$

$$Cl(g) + H_2(g) \xrightarrow{k_2} HCl(g) + H(g)$$

$$H(g) + Cl_2(g) \xrightarrow{k_3} HCl(g) + Cl(g)$$

$$2\,Cl(g) + M(g) \xrightarrow{k_4} Cl_2(g) + M(g)$$

Label the initiation, propagation, and termination steps. Derive the rate law for this reaction. Use the following bond dissociation data to explain why it is reasonable not to include the analogous inhibition steps in the mechanism that are included for the chain reaction involving $Br_2(g)$.

Molecule	H_2	HBr	HCl	Br_2	Cl_2
$D_0/\mathrm{kJ\,mol^{-1}}$	432	363	428	190	239

4. Carbonic anhydrase catalyzes the reaction $H_2O(l)+CO_2(g) \rightleftharpoons H_2CO_3(aq)$· Data for the reverse dehydration reaction using a total enzyme concentration of $2.32 \times 10^{-9}\,\mathrm{mol\,dm^{-3}}$ are given below.

$v/\mathrm{mol\,dm^{-3}\,s^{-1}}$	1.05×10^{-5}	2.22×10^{-5}	3.45×10^{-5}	4.17×10^{-5}
$[H_2CO_3]_0/10^{-3}\mathrm{mol\,dm^{-3}}$	2.00	5.00	10.00	15.00

Use the Lineweaver-Burk method to determine the values of K_m, the Michaelis constant, and k_2, the rate of product formation from the enzyme substrate complex.

5. The HF(g) chemical laser is based on the reaction $H_2(g) + F_2(g) \longrightarrow 2HF(g)$. The mechanism for this reaction involves the elementary steps

$$F_2(g) + M(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2F(g) + M(g) \quad \Delta_r H^\circ = -159\,\mathrm{kJ\,mol^{-1}} \tag{1}$$

$$F(g) + H_2(g) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HF(g) + H(g) \quad \Delta_r H^\circ = 134\,\mathrm{kJ\,mol^{-1}} \tag{2}$$

$$F(g) + H(g) \xrightarrow{k_3} HF(g) + F(g) \quad \Delta_r H^\circ = -411\,\mathrm{kJ\,mol^{-1}} \tag{3}$$

Comment on why the reaction $H_2(g) + M(g) \longrightarrow 2H(g) + M(g)$ is not included in the mechanism of the HF(g) laser even though it produces a reactant that could paricipate in step (3) of the reaction mechanism. Derive the rate for $d[HF]/dt$ for the above mechanism assuming that the steady-state approximation can be applied to both intermediate species, F(g) and H(g).