SCIE1000, Tutorial Week 12: Second-order chemical reactions.

- This week you will first work through some calculation and discussion questions relating to modelling second-order chemical reactions, and then an estimation question from the final exam in 2010. The chemical reaction questions are useful practice for the type of question on the exam – you will be presented with unfamiliar scenarios and asked to solve questions regarding the scenarios.
- You should have started preparing for the final exam. Remember that it is open-book. What materials will you take in? Do you need to re-write any key points in short, easily accessible form? There are no memory questions on the exam, so don't try to comit things to memory. Have a look at previous papers, particularly from Semester 1, 2010. Could you answer those questions, in 2 hours, if you didn't know what any of them were going to be? If not, then practise!

1 Questions

1. (Final exam, 2010. Worth 5 marks, so about 5 minutes to work.) The pH of Coca-Cola is about 2.5. Estimate the number of positive hydrogen ions (that is, H^+ ions) in Coca-Cola consumed by the Australian population each year. **Use units in your calculations and clearly state any values you assume.**

2. Chemical reactions can be classified according to the properties of their reaction rates, as:

   - **zero-order** if the reaction rate does not depend on the concentration of the reactant(s);
   - **first-order** if the reaction rate depends on the concentration of only one reactant;
   - **second-order** if the reaction rate depends on the square of the concentration of a single reactant, or the product of the concentrations of two reactants; and
   - **third-order** if the reaction rate depends on the product of the concentrations of three reactants.

   In lectures we have seen examples of zero-order reactions (for example, the metabolism of alcohol in the liver is effectively a zero-order reation) and first-order reactions (such as metabolism of most other drugs). Consider the following second-order reaction – the formation of gaseous hydrogen iodide (molecular formula HI, molar mass 127.9 g/mol^{-1}) from gaseous hydrogen and iodine:

   $$\mathrm{H}_2(g) + \mathrm{I}_2(g) \longrightarrow 2\ \mathrm{HI}(g)$$

   Let $[H_2](t)$, $[I_2](t)$ and $[HI](t)$ be the concentrations of hydrogen, iodine and hydrogen iodide at any time t in seconds, with the initial concentrations of H_2 and I_2 equal. Then these concentrations satisfy the system of equations

   $$[H_2]' = -k\,[H_2][I_2] \qquad [I_2]' = -k\,[H_2][I_2] \qquad [HI]' = 2k\,[H_2][I_2]$$

   where k is the reaction rate. (Note that $[H_2][I_2]$ means the concentration of hydrogen **multiplied by** the concentration of iodine, whereas $[HI]$ means the concentration of hydrogen iodide.)

   (a) Interpret briefly, in words, what each equation in this system of DEs is saying. In particular, interpret the physical meaning of the terms containing $[H][I]$.

   (b) If you examine these equations you will see that at any time, $[H_2]' + [I_2]' = -[HI]'$. What does this mean, and why is it expected?

   (c) If the concentration of reactants and products is measured in mol L^{-1} and the most appropriate unit of time for the above reaction is seconds, what are the units of k? (Show working.)

Chemical reactions rarely, if ever, proceed to completion (that is, a state in which the concentration of one or more of the reactants reaches zero). Instead, the reaction typically reaches a state called *chemical equilibrium*, where the concentrations of reactants and products remains constant with respect to time. In other words, reactions are occurring in *both* directions, with reactant(s) R transforming into product(s) P, and the product(s) P themselves becoming reactant(s) which react to produce new product(s) R. Consider again the formation of gaseous hydrogen iodide, but in terms of both the forward and reverse reactions.

$$\mathrm{H}_2(g)+\mathrm{I}_2(g) \rightleftharpoons 2\,\mathrm{HI}(g)$$

Let $[H_2](t)$, $[I_2](t)$ and $[HI](t)$ be the concentrations of hydrogen, iodine and hydrogen iodide at any time t in minutes (with the initial concentrations of H_2 and I_2 equal). Then these concentrations satisfy the system of equations

$$\begin{aligned}
[H_2]' &= -k_f\,[H_2][I_2] + k_r\,[HI]^2 \\
[I_2]' &= -k_f\,[H_2][I_2] + k_r\,[HI]^2 \\
[HI]' &= 2k_f\,[H_2][I_2] - 2k_r\,[HI]^2
\end{aligned}$$

where k_f is the forward reaction rate and k_r is the reverse reaction rate.

(d) Find the values of $[H_2]'$, $[I_2]'$ and $[HI]'$ at Equilibrium.

(e) Show why the following is true at equilibrium and explain in words what this means: $k_f[H_2][I_2] = k_r[HI]^2$.

For a given reaction at equilibrium, scientists can define an equilibrium constant, K. One reason that the equilbrium constant is of significance is that at a given temperature, regardless of the initial concentrations of reactants and products in the system, the equilibrium constant will remain the same. In other words there is one equilibrium constant for a given system at a particular temperature. Consider the following reaction type:

$$x\mathrm{A} + y\mathrm{B} \rightleftharpoons z\mathrm{C}$$

where A, B and C represent the reactants and products and x,y and z are coefficients. The equilibrium constant, K, for such a reaction is given by:

$$K = \frac{([C]_e)^z}{([A]_e)^x([B]_e)^y}$$

Note that the concentrations of reactants and products in this equation are those at equilibrium.

(f) Calculate the equilibrium constant for the formation of gasesous hydrogen iodide if at 700K, $k_f = 6.3 \times 10^{-2}$ and $k_r = 1.8 \times 10^{-3}$. (Hint: use Part (e).)

(g) Predict the equilibrium concentrations of H_2, I_2 and HI given the following inital concentrations at 700K:

$$[H_2]_0 = 1 \text{ mol L}^{-1} \quad [I_2]_0 = 1 \text{ mol L}^{-1} \quad [HI]_0 = 0 \text{ mol L}^{-1}$$

(Hint: the number of molecules in the system is constant.)

The end