

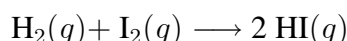
SCIE1000, Tutorial Week 12: Second-order chemical reactions.

- 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 commit 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 reaction) 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:



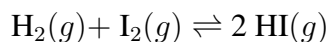
Let $[H_2](t)$, $[I_2](t)$ and $[HI](t)$ be the concentrations of hydrogen, iodine and hydrogen iodide at any time t in seconds, with the initial concentrations of H_2 and I_2 equal. Then these concentrations satisfy the system of equations

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

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.



Let $[\text{H}_2](t)$, $[\text{I}_2](t)$ and $[\text{HI}](t)$ 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

$$[\text{H}_2]' = -k_f [\text{H}_2][\text{I}_2] + k_r [\text{HI}]^2$$

$$[\text{I}_2]' = -k_f [\text{H}_2][\text{I}_2] + k_r [\text{HI}]^2$$

$$[\text{HI}]' = 2k_f [\text{H}_2][\text{I}_2] - 2k_r [\text{HI}]^2$$

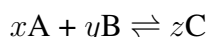
where k_f is the forward reaction rate and k_r is the reverse reaction rate.

(d) Find the values of $[\text{H}_2]'$, $[\text{I}_2]'$ and $[\text{HI}]'$ at Equilibrium.

(e) Show why the following is true at equilibrium and explain in words what this means:

$$k_f [\text{H}_2][\text{I}_2] = k_r [\text{HI}]^2.$$

For a given reaction at equilibrium, scientists can define an equilibrium constant, K . One reason that the equilibrium 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:



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:

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

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

(f) Calculate the equilibrium constant for the formation of gaseous 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 initial concentrations at 700K:

$$[\text{H}_2]_0 = 1 \text{ mol L}^{-1} \quad [\text{I}_2]_0 = 1 \text{ mol L}^{-1} \quad [\text{HI}]_0 = 0 \text{ mol L}^{-1}$$

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

The end