

Reaction Kinetics: Elementary Ideas

10th February 2010

1 Introduction

Chemical equilibrium deals with chemical systems at *equilibrium*: that is, concentrations (and thus amounts) of chemical species do not change with time.

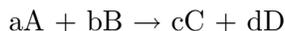
Chemical reaction kinetics attempts to describe the way a non-equilibrium system changes with time in order to achieve chemical equilibrium (of course, with this is tied thermal, mechanical equilibrium)

To reiterate:

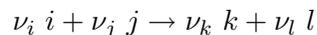
1. thermodynamics tells us whether the free energy associated with a chemical transformation dictates whether the transformation occurs.
2. kinetics tells us how fast (what is the rate) of that transformation towards an equilibrium state. (what is the concentration of a specie(s) as a function of time)

2 Reaction Rates

Consider a generic representation of a chemical reaction:



We want to know the amount of A, B, C, and D as the process moves along. Let's consider some "reaction extent" variable (an abstraction to allow us to speak of how far the reaction has proceeded *independent of the reaction stoichiometry*). The **positive-valued** variable is *arbitrarily* named ζ . We rewrite the expression above in an equivalent form:



We can write the amount of a particular species remaining in the reaction vessel at a particular instant as:

$$n_i = n_i^o + \nu_i \zeta$$

This suggests that ν_i has an associated **sign**.

- Reactant: $\nu_i < 0$
- Product: $\nu_i > 0$
- These definitions thus lead to decreasing reactant and increasing product amounts in our expression above for n_i . Recall ζ is positive.

The rate of change of species "i" is thus a differential:

$$\frac{dn_i}{dt} = \nu_i \frac{d\zeta}{dt}$$

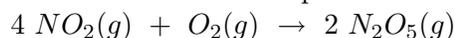
We stop here to formally define the **reaction rate** as:

$$\begin{aligned} \text{Rate} &= \frac{d\zeta}{dt} \\ \text{Rate} &= \frac{1}{\nu_i} \frac{dn_i}{dt} \end{aligned}$$

The *Rate of Reaction* is defined as:

$$\text{Rate} = \frac{-1}{a} \frac{dn_A}{dt} = \frac{-1}{b} \frac{dn_B}{dt} = \frac{1}{c} \frac{dn_C}{dt} = \frac{1}{d} \frac{dn_D}{dt}$$

Let's consider an example:



The rate for this reaction is expressed as:

$$\text{Rate} = \frac{-1}{4} \frac{dn_{\text{NO}_2}}{dt} = -1 \frac{dn_{\text{O}_2}}{dt} = \frac{1}{2} \frac{dn_{\text{N}_2\text{O}_5}}{dt}$$

Note that the rate as written in terms of species amounts is not independent of the stoichiometric coefficients used. Thus, these must be specified and consistently maintained throughout the kinetic analysis.

Furthermore, there is a size extensivity issue relating to the fact that if we double the reaction vessel volume, the rates will change (i.e., doubling the amount of species "i" will lead to twice the rate. To convert the rate to an **intensive** entity, we can divide by the volume of the system:

$$R = \frac{Rate}{V} = \frac{1}{V} \left(\frac{1}{\nu_i} \frac{dn_i}{dt} \right) = \frac{1}{\nu_i} \frac{d[i]}{dt}$$

Thus, to summarize, we now have a relation to define for us a rate of a reaction in terms of the instantaneous rate of change of the species involved. We need some explicit relation that includes the instantaneous concentrations of species to fully be able to use this formalism. We turn to that next.