**Reaction Rates and Composition Changes**

We’ve derived reaction rates as collisions that lead to reaction so that:

**Reaction Rate = Collision Rate * Fraction of Collisions leading to reaction**

Collision rate of a species A with a species B, was derived as: \( \Theta_{AB} = n_A n_B \pi \sigma^2 (g) \)

With the units being collisions per unit volume per unit time.

The reaction rate is then some fraction of the collision rate, e.g. Const*\( \Theta_{AB} \), with the units the same as the collision rate.

If we assume some generic product C, such that \( A + B \rightarrow C \), then, the reaction rate is also the rate of destruction of species A and species B per unit volume per unit time as a result of this particular reaction. It is also the rate of production of species C as a result of this particular reaction.

If we use the Arrhenius form of the reaction rate, i.e. \( n_A n_B k \), where \( k = AT^n e^{-EA/RT} \), then we can write the following:

\[
\frac{-dn_A}{dt} = \frac{-dn_B}{dt} = \frac{dn_C}{dt} = k n_A n_B \tag{1}
\]

But it’s important to remember that this change in number densities is only the contribution due to one specific reaction. There may be other contributors to the change in these number densities, most importantly: other reactions, and changes in pressure, temperature, volume, or total number of species that affect the local thermodynamic state. For example, if the flow is expanding as it reacts, the number density of all species will be driven downward, irrespective of the effect of reaction rate.

A special case is for constant volume. We often define concentration as moles per unit volume, so \( c_A = n_A/V = n_A/N_{Avo} = [A] \). Multiplying our rate equation by Avogadro’s number, we get:

\[
-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = k[A][B] \tag{2}
\]

Which is the most common form we see in reaction rate analysis. However, it still represents only the concentration change due to reaction – not other effects. If we recast the equation in terms of mole numbers and volumes, then we get:
\[-\frac{d}{dt} \left( \frac{N_A}{V} \right) = -\frac{d}{dt} \left( \frac{N_B}{V} \right) = \frac{d}{dt} \left( \frac{N_C}{V} \right) = \frac{kN_AN_B}{V^2} \quad (3)\]

Note that the left hand side terms can be cast as, for example:

\[\frac{d}{dt} \left( \frac{N_C}{V} \right) = \frac{1}{V} \frac{dN_C}{dt} - \frac{N_C}{V^2} \frac{dV}{dt} \quad (4)\]

Now the right hand side of equation (3) only contributes to the 2\textsuperscript{nd} term on the right hand side of equation (4), so that equation (3) can only be used rigorously when volume is constant, such that the first term on the RHS of (4) is zero. In addition, equation (3) still remains only the contribution to species changes due to that one reaction. Any other reactions of species A, B, and C would contribute to the \(d[A]/dt\), \(d[B]/dt\), and \(d[C]/dt\) equations.