The law of mass action only rigorously applies to elementary reactions (in that otherwise the exponents do not match stoichiometric coefficients). These are reactions whose equations match which particles are colliding on the microscopic scale. Consider the reaction

\[
\ce{r_1 R_1 + r_2 R_2 + \ldots + r_n R_n <=> p_1 P_1 + p_2 P_2 + \ldots + p_m P_m}\]

Reaction \((1)\) is elementary if and only if it proceeds in a single step. At some time \(t = t_c\) all reactant particles \(\ce{R_1, R_2, \ldots, R_n}\) collide. Quantum mechanically this collision is not too well defined, so view it to be Newtonian in essence. Not to mention: the probability \(P\) of the simultaneous collision goes to zero as \(n \to \infty\). This is why in actuality most elementary steps involve at most three individual constituents.

We therefore sacrifice some generality and instead consider the easier to handle

\[
\ce{R_1(g) + R_2(g) <=> P_1(g) + P_2(g)}\]

The reactant molecules must collide in order for a reaction to take place. Therefore we must know the collision frequency in order to determine the reaction rate. This rate must be the product of some probability and the collision frequency. **Collision Theory** gives a way to calculate this collision frequency. In doing so Maxwell-Boltzmann distributions are used to calculate the ratio of atoms that can react within a given concentration. Most of this ‘stuff’ gets swept up in the reaction rate constant.

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**Energies**

Collision theory postulates that particles only initiate a transformation when they have enough energy. This is called *activation energy* and denoted by \(E_a\). Maxwell-Boltzmann distribution

\[
\frac{\mathrm{d}N_v}{N} = 4\pi\left(\frac{m}{2\pi k_bT}\right)^{3/2}v^2\exp\left(-\frac{mv^2}{2k_bT}\right)\mathrm{d}v
\]

allows us to estimate the fraction of particles that have the required amount of movement. Note we are technically assuming \(\text{total energy} = \text{kinetic energy}\). Similarly relativistic effects are ignored, and no cap is placed on maximum velocity. With these simplifications, the fraction of interesting particles is

\[
f = \frac{N^*}{N} = \frac{1}{k_bT}\int_{E_a}^\infty\exp\left(-\frac{E}{k_bT}\right)\mathrm{d}E
\]

which evaluates to

\[
\int E_a^\infty\exp\left(-\frac{E}{k_bT}\right)\mathrm{d}E\label{3'}
\]

---

**Number of interesting collisions**

Say \((Z^*)\) is the number of collisions that matter. We will look for a function \(Z\) such that

\[
Z^* = Z\cdot f\label{4}\]

\[
Z^* = Z\cdot \exp\left(-\frac{E_a}{k_bT}\right)\]

\[
Z^* = Z\cdot \text{cdot f. label {4}}\]
The Maxwell-Boltzmann distribution (Equation \(\ref{2}\)) gives for a single kind of particle (say two \(\ce{R1}\)'s) that there are

\[
Z = 2N^2 \left( \sigma_{\ce{R1}} \right)^2 \sqrt{\frac{\pi RT}{M_{\ce{R1}}}} \label{5}
\]

collisions in \(1\) second per \(1\ \text{cm}^3\) if \(N\) is the number of particles per square centimeter. (This is the traditional starting point unit.) Hence the rate of such a reaction would be

\[
v_r = \frac{2Z^*}{N_A} \cdot 10^3 \left(\frac{\text{mol}}{\text{s} \cdot \text{dm}^3}\right). \label{6}
\]

Reaction rate \((v_r)\)

If you like, you are now able to substitute \((f)\) from Equation \(\ref{3'}\) and \((Z)\) via Equation \(\ref{5}\) into Equation \(\ref{4}\). Then insert Equation \(\ref{4}\) into Equation \(\ref{6}\). After necessary manipulation, this yields Equation \(\ref{7}\).

\[
v_r = \underbrace{4 \times 10^{-3} N_A \left(\sigma_{\ce{R1}}\right)^2 \sqrt{\frac{\pi RT}{M_{\ce{R1}}}} \exp\left(-\frac{E_a}{k_bT}\right)}_k \cdot \overbrace{\left(\frac{N}{N_A} \cdot 10^3\right)^2}^{c^2}. \label{7}
\]

Coming back to our actual reaction (Equation \(\ref{1'}\)) involves more relative quantities. For example, \(\sigma_{\ce{R1}}\) becomes

\[
\sigma_{\text{aver}} = 0.5\left(d_{\ce{R1}} + d_{\ce{R2}}\right).
\]

So it is a bit more difficult. But the result is analogous to Equation \(\ref{7}\).

\[
v_r = \underbrace{2\sqrt{2} \times 10^{-3} N_A \left(\sigma_{\text{aver}}\right)^2 \sqrt{\pi RT\left(\frac{1}{M_{\ce{R1}}} + \frac{1}{M_{\ce{R2}}}\right)}}_k \cdot c_{\ce{R1}} \cdot c_{\ce{R2}}
\]

More compactly, if \(\ce{R1} = A\) and \(\ce{R2} = B\)

\[
v_r = k[A][B] \label{8}
\]

which is what we set out to prove.

• This derivation assumes that every active collision leads to a reaction. When theoretically computed \(k\) were compared to experimental, an extra factor was introduced, \(P\). This is called the steric factor, and in classical collision theory \(P\) remains empirical in essence.

Collision theory is for elementary steps

As your quote suggests, collision theory is a first theoretical explanation for the proportionality to products of concentrations. It does not generally explain various exponentiation. It does not have to either. The higher (or non-integer or negative) exponents usually derive from the mechanism itself. In other words, the fact that common reactions are not elementary comes into play.
For instance, the transition
\[
\ce{2Br- + H2O2 + 2H+ -> Br2 + H2O}
\]
is experimentally found to follow
\[
v_r = k\ce{[H2O2][H+][Br^-]} \label{a}.
\]
Mathematically, we can verify that one possible mechanism is
\[
\ce{H+ + H2O2 <=>[K] H2O+-OH}, \tag{fast equilibrium}
\]
\[
\ce{H2O+-OH + Br- ->[k_2] HOBr + H2O}, \tag{slow}
\]
\[
\ce{HOBr + H+ + Br- ->[k_3] Br2 + H2O}, \tag{fast}
\]
Indeed,
\[
K_c = \frac{\ce{[H2O+-OH]}}{\ce{[H+][H2O2]}} \implies \ce{[H2O+-OH]} = K_c\ce{[H+][H2O2]} \label{b}.
\]
Applying the method of stationary concentration gives
\[
v(\ce{HOBr}) = 0 \implies k_2\ce{[H2O+-OH][Br-]} = k_3\ce{[H2O2][H+][Br-]} \label{c}.
\]
The overall rate of the reaction is characterised by the rate of formation of bromine \(\ce{Br2}\). So,
\[
v_r = k_3\ce{[H2O2][H+][Br-]} \overset{(c)}{=} k_2K_c\ce{[H+][H2O2][Br^-]} \overset{(b)}{=} k_2K_c \label{d}.
\]
This only shows that it might be a valid mechanism, not that the reaction actually follows such a pathway. Therefore, while we can use collision theory to derive the law of mass action as a first approximation, the exponents for non-elementary reactions are determined via experiment.

**Contributors**
- [Linear Christmas](https://stackoverflow.com/users/3358113/linear-christmas) (StackExchange)