Macroscopic Reaction Rates from Microscopic Properties

Bimolecular Reactions – Collision Theory

A+B→C

From kinetic theory, we found A—B collision rate in a gas:

$$Z_{AB} = \pi d_{AB}^2 \left(\frac{8k_BT}{\pi\mu_{AB}}\right)^{1/2} N_A N_B \qquad (\text{cm}^{-3}\ \text{sec}^{-1})$$
$$= \sigma_{gas-kinetic} \cdot \overline{v} \cdot N_A N_B$$

[**Note on notation**: to distinguish Boltzmann constant *k* from rate coefficient *k*, we will write the former as k_B!]

Reaction rate $\dfrac{d[C]}{dt} = k[A][B]$

Can we simply identify rate constant *k* with gas-kinetic collision rate $\sigma\ v_{AB}$?

NO – typically $k \ll \sigma\ v_{AB}$

k has Arrhenius type behavior, $\exp(-E_{act}/RT)$, which does not appear anywhere in the expression for gas kinetic collision frequency

Arrhenius behavior suggests reactive cross section, σ_R, has energy dependence $\sigma_R(E)$ or equivalently, velocity dependence $\sigma_R(v_{AB})$.

$$dZ_{reactive} \propto N_A N_B \sigma_R(v_{AB}) v_{AB} f(v_{AB}) 4\pi v_{AB}{}^2 dv_{AB}$$

or

$$\frac{Z_{reactive}}{N_A N_B} = k = \int_0^\infty v_{AB}\sigma_R(v_{AB}) f(v_{AB}) 4\pi v_{AB}{}^2 dv_{AB}$$

$$k = \left(\frac{\mu_{AB}}{2\pi k_B T} \right)^{3/2} \int_0^\infty v_{AB} \sigma_R(v_{AB}) e^{-\mu v_{AB}{}^2/2k_BT} 4\pi v_{AB}{}^2 dv_{AB}$$

In terms of relative kinetic energy, E= $\frac{1}{2}\mu v_{AB}{}^2$

$$k = \frac{1}{k_B T} \left(\frac{8}{\pi \mu_{AB} k_B T} \right)^{1/2} \int_0^\infty E \sigma_R(E) e^{-E/k_BT} dE$$

Now we just need an expression for $\sigma_R(E)$ or $\sigma_R(v_{AB})$.

Hard-Sphere limit:

$$P_{react} = 1, r_{\min} \le d_{AB}$$
$$P_{react} = 0, r_{\min} > d_{AB}$$

$$\sigma_R(E) = \pi d_{AB}^2$$

$$k(T) = \left(\frac{\mu_{AB}}{2\pi k_B T} \right)^{3/2} \pi d_{AB}^2 \int_0^\infty v_{AB} e^{-\mu v_{AB}{}^2/2k_BT} 4\pi v_{AB}{}^2 dv_{AB}$$

$$k(E) = \bar{v} \cdot \sigma_R = \left(\frac{8 k_B T}{\pi \mu_{AB}} \right)^{1/2} \pi d_{AB}^2$$

Estimate the magnitude of this expression:

$$d_{AB} \approx 4 \times 10^{-8} cm$$
$$v \approx 5 \times 10^4 cm/s, \quad 300K$$

$$k \approx 5 \times 10^{-10} cm^3 molecule^{-1} \sec^{-1}$$
$$\approx 1.5 \times 10^{11} L\ mole^{-1} \sec^{-1}$$

$t_{1/2}$ would be on the order of 10^{-11} seconds at p = 1 bar (or c=1M)!
Also predicted temperature dependence of k is $T^{1/2}$

What's missing??

Reactive Hard Sphere Model

Both Arrehenius temperature dependence and energy profile for a reaction suggest an energy requirement for reaction to occur.

One possibility,

$$\sigma_R = 0,\ \text{if E<E}_0$$
$$\sigma_R = \pi d_{AB}^2,\ \text{if E>E}_0$$

But look at three situations with same kinetic energy E:

(i) Impact parameter b=0; maximum impact
(iii) Impact parameter, b≥ d_{AB}, no collision occurs at all

Therefore we need a more detailed "dynamical" model.

"Energy along line of centers" ("Old Collision Theory")

Partition energy into

- "along line of centers", $E_C = E\left(1-\dfrac{b^2}{d_{AB}}\right)$, if , b ≤ d_{AB}
- "tangent to the line of centers", E_t

$$E_C = \frac{1}{2}\mu_{AB}\left(v_\perp\right)^2; \quad v_\perp = v\cos\phi; \quad E_t = \frac{1}{2}\mu_{AB}\left(v_\parallel\right)^2$$

$$E_C = \frac{1}{2}\mu_{AB}v^2\cos^2\phi = \frac{1}{2}\mu_{AB}v^2\left(1-\sin^2\phi\right) = E\left(1-\sin^2\phi\right)$$

$\sin\phi = b/d_{AB}$, thus
$$E_C = E\left(1-\frac{b^2}{d_{AB}^2}\right), \quad \left(b \le d_{AB}\right)$$
$$E_C = 0, \quad \left(b > d_{AB}\right)$$

If $E < E_0$ of course, $E_C < E_0$, $P_{react}(E)=0$, $\sigma_R(E)=0$

For any collision energy $E > E_0$, there is some critical impact parameter b_0 for which

$$E_C = E\left(1-\frac{b^2}{d_{AB}^2}\right) = E_0$$

$$b_0^2 = d_{AB}^2\left(1-\frac{E_0}{E}\right)$$

Assume: all collisions with $b < b_0$ (at energy $E > E_0$) are reactive

Thus

$$\sigma_R(E) = \pi b_0^2 = \pi d_{AB}^2\left(1-\frac{E_0}{E}\right) \qquad \text{for } E \ge E_0$$

$$\sigma_R = 0 \qquad \text{for } E < E_0$$

Now we only need to insert in previous expression to find k(T).

$$k = \frac{1}{k_B T}\left(\frac{8}{\pi\mu_{AB}k_B T}\right)^{1/2} \int_0^\infty E\sigma_R(E)e^{-E/k_B T}dE$$

$$= \frac{1}{k_B T}\left(\frac{8}{\pi\mu_{AB}k_B T}\right)^{1/2} \int_{E_0}^\infty E\pi d_{AB}^2\left(1-\frac{E_0}{E}\right)e^{-E/k_B T}dE$$

$$= \frac{1}{k_B T}\left(\frac{8}{\pi\mu_{AB}k_B T}\right)^{1/2} \pi d_{AB}^2 \int_{E_0}^\infty (E-E_0)e^{-E/k_B T}dE$$

$$x = \frac{(E-E_0)}{k_B T}; \quad dx = \frac{dE}{k_B T}; \quad e^{-E/k_B T} = e^{-E_0/k_B T}e^{-x}$$

Thus

$$k = \left(\frac{8k_B T}{\pi\mu_{AB}}\right)^{1/2} \pi d_{AB}^2 e^{-E_0/k_B T}\int_0^\infty xe^{-x}dx$$

$$k = \left(\frac{8k_B T}{\pi\mu_{AB}}\right)^{1/2} \pi d_{AB}^2 e^{-E_0/k_B T}\int_0^\infty xe^{-x}dx; \quad \left(\int_0^\infty xe^{-x}dx = 1\right)$$

$$k = \left(\frac{8k_B T}{\pi\mu_{AB}}\right)^{1/2} \cdot \pi d_{AB}^2 \cdot e^{-E_0/k_B T}$$

(mean relative speed) (hard sphere gas kinetic speed) (Arrhenius-type factor with $E_0 \approx E_{act}$)

RELATIONSHIP BETWEEN E_0 (critical line of centers energy) and E_{act}, (empirical Arrhenius energy)

$$k = Ae^{-E_{act}/k_BT}$$

$$\frac{d\ln k}{dT} = \frac{d}{dT}\left(\ln A - \frac{E_{act}}{k_BT}\right) = \frac{E_{act}}{k_BT^2}$$

$$k^{CT} = \left(\frac{8k_BT}{\pi\mu_{AB}}\right)^{1/2} \pi d_{AB}^2 e^{-E_0/k_BT}$$

$$\frac{d\ln k^{CT}}{dT} = \frac{d}{dT}\left(\frac{1}{2}\ln\left(\frac{8k_BT}{\pi\mu_{AB}}\right) + \ln\left(\pi d_{AB}^2\right) - \frac{E_0}{k_BT}\right) = \frac{1}{2T} + \frac{E_0}{k_BT^2}$$

Now we require that:

$$\frac{d\ln k}{dT} = \frac{d\ln k^{CT}}{dT}$$

$$\frac{E_{act}}{k_BT^2} = \frac{1}{2T} + \frac{E_0}{k_BT^2}$$

$$E_{act} = \frac{1}{2}k_BT + E_0$$

How well does this theory work?

Predicted pre-exponential factor is:

$$\pi d_{AB}^2 \left(\frac{8k_BT}{\pi\mu_{AB}}\right)^{1/2} \approx \left(3\times10^{-15}\,cm^2\right)\left(4\times10^4\,cm/s\right) \approx 10\times10^{-11}\,cm^3/\text{sec}$$

or about $6\times10^{10}\,L/mol\cdot s$

In most cases, A(T) is much smaller in magnitude!

Some examples:

Reaction	E_{act}, kJ/mol	Measured $Log_{10}(A/T^{1/2})$	Calculated $Log_{10}(Z'_{AB}/T^{1/2})$	P
$CH_3+CH_3 \rightarrow C_2H_6$	0.0	9.32	9.78	0.35
$Cl+H_2 \rightarrow HCL+H$	21	9.69	10.38	0.20
$NO+O_3 \rightarrow NO_2+O_2$	28	8.60	9.89	0.05
$CH_3+C_2H_6 \rightarrow CH_4+C_2H_5$	43.5	6.99	10.03	0.0009

Clearly the bimolecular rate constant < (sometimes <<) the gas-kinetic collision rate constant, even after accounting for activation energy.

Sometimes this is represented by a steric factor $p=A/Z_{AB}$

So $$k^{(corrected)} = p \cdot \pi d_{AB}^2 \cdot \left(\frac{8k_BT}{\pi\mu_{AB}}\right)^{1/2} \cdot e^{-E_0/k_BT}$$

But p is strictly a "fudge factor'!

(In a little while, we will give a recipe for fudge.)