COMMONWEALTH OF AUSTRALIA

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Kinetics: Elementary processes and reaction mechanisms

Lecture 30

Liquids: Chemical kinetics

Lecture 31

Kinetics: Elementary processes and reaction mechanisms

Lecture 32

Surface and interfacial tension

Rate laws – a few reminders

In chemical kinetics we are interested in determining how the concentration of a species changes over time as we proceed from an initial state to equilibrium. This may be expressed as EITHER:

A differential rate law, showing the rate of change of concentration as a function of concentrations of one or more species. E.g. $\frac{d[A]}{dt} = -k[A]$ $\frac{\mathrm{d}[\mathrm{HBr}]}{\mathrm{d}t} = \frac{k_a[\mathrm{H_2}][\mathrm{Br_2}]^{\frac{3}{2}}}{[\mathrm{Br_2}] + k_b[\mathrm{HBr}]}$

OR, an integrated rate law, showing concentration as a function of time. E.g. $[A] = [A]_0 \exp(-kt)$

If we know the differential rate law, then we can determine the integrated rate law analytically for simple cases, or numerically otherwise.

E.g. If the reaction A → B has a simple "first order" rate law: $\frac{d[A]}{dt} = -k[A]$

We can integrate this expression to give [A] as a function of time: $\int \frac{d[A]}{[A]} = \int -k dt$

$[A] = [A]_0 \exp(-kt)$

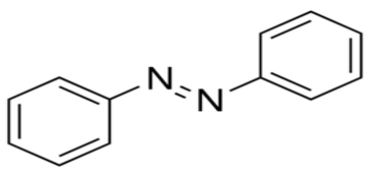
Reminder: Chemical reactions as trajectories

We saw last lecture that for an elementary process which passes in a trajectory over a *single* transition state, the size of a rate coefficient is determined by the microscopic dynamics of the molecules involved and depends strongly on temperature.

Only some reactions can be described as an elementary process. They include things like bond stretching (and then breaking), bond forming, or the internal rotation of groups about a bond.

e.g. Dissociation A → B + C (like $H_2(g) \rightarrow 2H(g)$, or $HI(g) \rightarrow H(g) + I(g)$)

e.g. Isomerization Does cis-trans isomerization in azobenzene occur by rotation around –N=N– or inversion (a 180° N=N-C angle)?



Elementary Processes

Elementary processes are unimolecular or bimolecular events between molecules in the reacting system. (Other processes like termolecular collisions are too rare to be significant.) Some examples:

- A → B (unimolecular reaction)
- A → B + C (unimolecular dissociation)

$$\frac{d[A]}{dt} = -k[A]$$

- A + B → C (bimolecular reaction)
- A + B → C + D (bimolecular reaction)

$$\frac{d[A]}{dt} = -k[A][B]$$

If a step is genuinely elementary, the microscopic rate law ***can*** be inferred: the order is based entirely on the molecularity.

Other reactions are the combination of a sequence of multiple elementary steps… what can we do with these?

Rate laws Depend on the Reaction Mechanism

A balanced chemical equation gives us the relative proportions of reactants and products.

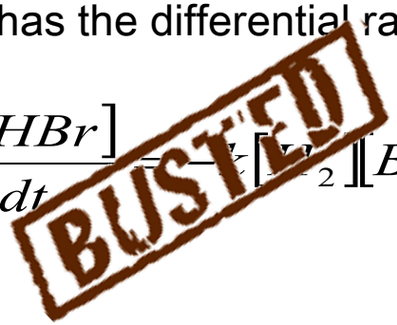
It does not give us the rate law for the reaction!

Example? The gas-phase reaction $H_2 + Br_2 \rightarrow 2HBr$ which has the differential rate law:

$$\frac{d[HBr]}{dt} = \frac{k_a[H_2][Br_2]^{\frac{3}{2}}}{[Br_2] + k_b[HBr]}$$

NOT

$$\frac{d[HBr]}{dt} = -k[H_2][Br_2]$$



A complicated rate law like the one above is not an isolated example:

many reactions have rate laws that cannot be described by a simple linear response approach.

In general, in order to determine a rate law, we need to understand the reaction mechanism, which describes molecular transformations as a series of elementary processes.

Testing Schemes of Elementary Processes

How do we know which elementary processes occur in a mechanism? In general, this is difficult to establish. We may have some knowledge from:

- Elementary processes found to occur in previous experiments
- Theoretical calculations of elementary steps

But we often simply need to test many schemes involving the simplest types of elementary processes and see if they give us the observed kinetics.

Multiple elementary kinetic schemes can predict the same overall rate equations. This means the best we can do is say that a particular scheme is *consistent with* the data. (If it is *not consistent* with the data, we can throw away that kinetic scheme.)

Worksheet time

Testing Schemes of Elementary Processes

To simplify the analysis for this kind of problem, some common approximations are:

- The Steady State Approximation – assume all reactive intermediates quickly reach an unchanging “steady state” concentration, e.g. d[NO]/dt = 0

- Identifying a Rate-Determining Step – the slowest bottleneck in a reaction scheme often determines the overall rate

- Merging any fast-reacting reversible reactions into a pre-equilibrium which stays in equilibrium even as one of the products slowly leaks away into subsequent steps, e.g. $N_2O_5 \leftrightharpoons NO_2 + NO_3$

Kinetics and Chemical Equilibrium

Seeing that the kinetics of a reaction can involve some complicated sequence of elementary processes, possibly involving chemical species other than those identified as reactants or products, how do we connect the kinetics with the equilibrium state?

For example: $2NO + 2H_2 \leftrightharpoons N_2 + 2H_2O$ — Overall balanced reaction

is believed to occur as

i) $NO + NO \underset{k_1}{\overset{k_{-1}}{\leftrightharpoons}} N_2O_2$ — Bimolecular NO + NO collision; Unimolecular N_2O_2 decomposition

ii) $N_2O_2 + H_2 \underset{k_2}{\overset{k_{-2}}{\leftrightharpoons}} N_2O + H_2O$ — Bimolecular N_2O_2 + H_2 collision; Bimolecular N_2O + H_2O collision

iii) $N_2O + H_2 \underset{k_3}{\overset{k_{-3}}{\leftrightharpoons}} N_2 + H_2O$ — Bimolecular N_2O + H_2 collision; Bimolecular N_2 + H_2O collision

At equilibrium, the forward and backward rate of *each elementary process* must be equal. This requirement is known as the principle of detailed balance. i.e.

$k_1[NO]^2_{eq} = k_{-1}[N_2O_2]_{eq}$, $k_2[N_2O_2]_{eq}[H_2]_{eq}=k_{-2}[N_2O]_{eq}[H_2O]_{eq}$ and $k_3[N_2O]_{eq}[H_2]_{eq}=k_{-3}[N_2]_{eq}[H_2O]_{eq}$

$$\Rightarrow \frac{k_1k_2k_3}{k_{-1}k_{-2}k_{-3}} = \frac{[N_2O_2]_{eq}}{[NO]^2_{eq}} \frac{[N_2O]_{eq}[H_2O]_{eq}}{[N_2O_2]_{eq}[H_2]_{eq}} \frac{[N_2]_{eq}[H_2O]_{eq}}{[N_2O]_{eq}[H_2]_{eq}} = \frac{[N_2]_{eq}[H_2O]^2_{eq}}{[NO]^2_{eq}[H_2]^2_{eq}} = K$$

The equilibrium constant

Learning outcomes

After this lecture you should be able to:

- Explain how a postulated elementary kinetic scheme can be falsified by seeing whether it predicts the experimentally obtained rate law.
- Write down the differential equations for a postulated elementary reaction scheme and recognise various approximate conditions.
- Use detailed balance to obtain the equilibrium expression from kinetics.