# Numerical methods

# Review: models

Classifications

- Mechanistic / Statistical
- Deterministic / Stochastic
- Analytical / Computational

Reasons for computer methods (*iterative calculations*)

- Numerical integration
- Parameter estimation
- Data analysis

Reasons for modeling

- Prediction / Forecasting
- Understanding

Simulation → generate data

Data analysis → reduce amount of data

# Some common problems that require numerical solutions (not exclusive list)

- Constraint satisfaction (solving system of equations)
- Parameter estimation (“best fit” to data)
- Numerical integration (prediction / forecasting)

# Constraint satisfaction

# Constraint satisfaction

- Find set of values that satisfies a system of linear or nonlinear equations (i.e., “solve” the system of equations)

- Also falls under the umbrella of AI, operations research

- The system of equations can also be a set of logical statements (“logic programming”) but this is a separate domain

- Example: phase equilibria problem

Constraint satisfaction example

# Carbon dioxide-water equilibrium

Stoichiometric balance:

$$CO_{2(g)} + H_2O \rightleftharpoons CO_2{\cdot}H_2O$$
$$CO_2{\cdot}H_2O \rightleftharpoons H^+ + HCO_3^-$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

Total concentration:

$$[CO_2^T] = [CO_2{\cdot}H_2O] + [HCO_3^-] + [CO_3^{2-}]$$
$$= H_{CO_2} p_{CO_2} \left(1 + \frac{K_{c1}}{[H^+]} + \frac{K_{c1}K_{c2}}{[H^+]^2}\right)$$

Mass law expressions:

$$K_{hc} = H_{CO_2} = \frac{[CO_2 \cdot H_2O]}{p_{CO_2}}$$
$$K_{c1} = \frac{[H^+][HCO_3^-]}{[CO_2 \cdot H_2O]}$$
$$K_{c2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

Effective Henry's law constant:

$$H^*_{CO_2} = H_{CO_2}\left(\frac{K_{c1}}{[H^+]} + \frac{K_{c1}K_{c2}}{[H^+]^2}\right)$$

Note that

$$H^*_{CO_2} > H_{CO_2}$$

Concentrations:

$$[CO_2 \cdot H_2O] = H_{CO_2} p_{CO_2}$$
$$[HCO_3^-] = \frac{K_{c1}[CO_2 \cdot H_2O]}{[H^+]} = \frac{H_{CO_2} K_{c1} p_{CO_2}}{[H^+]}$$
$$[CO_3^{2-}] = \frac{K_{c2}[HCO_3^-]}{[H^+]} = \frac{H_{CO_2} K_{c1} K_{c2} p_{CO_2}}{[H^+]^2}$$

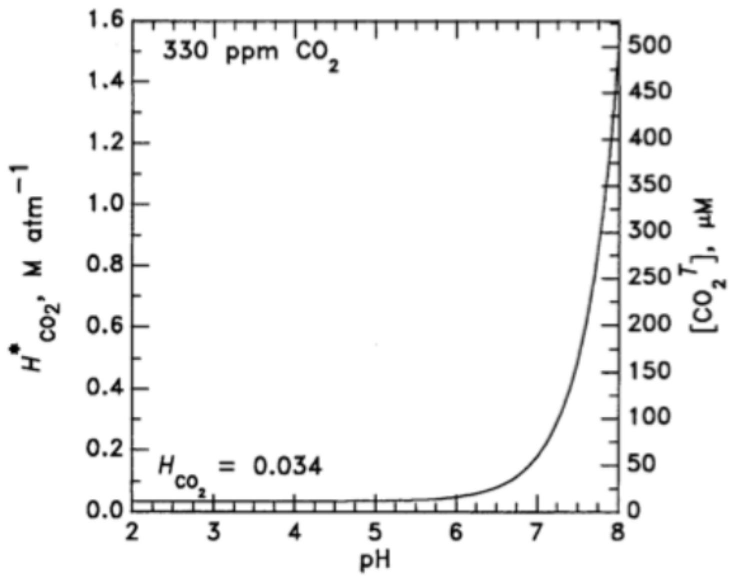



**FIGURE 7.4** Effective Henry's law constant for $CO_2$ as a function of the solution pH. Also shown is the corresponding equilibrium total dissolved $CO_2$ concentration $[CO_2^T]$ for a $CO_2$ mixing ratio of 330 ppm.

# Example: pH of "pure" rainwater

For a system containing only $CO_2$ with mixing ratio of $\xi_{CO_2}$ = 350 ppm and water at 298 K, what is the pH of cloudwater and rain droplets in this system (assume equilibrium between gas and condensed phase)?

Charge balance

$$[H^+] = [OH^-] + [HCO_3{}^-] + 2[CO_3{}^{2-}]$$

Replace concentrations with mass law relations:

$$[H^+] = \frac{K_w}{[H^+]} + \frac{H_{CO_2} K_{c1} p_{CO_2}}{[H^+]} + \frac{H_{CO_2} K_{c1} K_{c2} p_{CO_2}}{[H^+]^2}$$

Rearrange as a cubic equation,

$$[H^+]^3 - \left(K_w + H_{CO_2} K_{c1} p_{CO_2}\right) [H^+] - 2 H_{CO_2} K_{c1} K_{c2} p_{CO_2} = 0$$

$\Rightarrow$ *The solution pH is 5.6.*

**TABLE 7.4 Thermodynamic Data for Aqueous Equilibrium Constants**

| Equilibrium | $K$ at 298 K (M) | $\Delta H_A$ at 298 K, kcal mol$^{-1}$ |
|---|---|---|
| $H_2O \rightleftharpoons H^+ + OH^-$ | $1.0 \times 10^{-14}$ | 13.35 |
| $CO_2 \cdot H_2O \rightleftharpoons H^+ + HCO_3^-$ | $4.3 \times 10^{-7}$ | 1.83 |
| $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ | $4.7 \times 10^{-11}$ | 3.55 |
| $SO_2 \cdot H_2O \rightleftharpoons H^+ + HSO_3^-$ | $1.3 \times 10^{-2}$ | −4.16 |
| $HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$ | $6.6 \times 10^{-8}$ | −2.23 |
| $NH_3 \cdot H_2O \rightleftharpoons NH_4^+ + OH^-$ | $1.7 \times 10^{-5}$ | 8.65 |

$$p_{CO_2} = 350 \times 10^{-9} \text{ atm}$$

$$H_{CO_2} = 3.4 \times 10^{-2} \text{ M atm}^{-1}$$

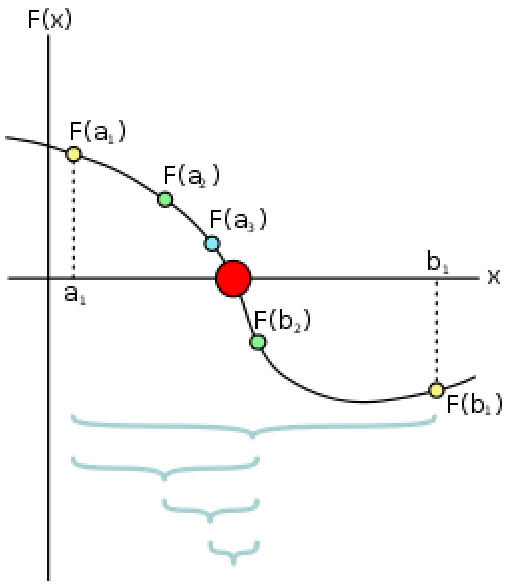
$$K_{c1} = 4.3 \times 10^{-7} \text{ M}$$

$$K_{c2} = 4.7 \times 10^{-11} \text{ M}$$

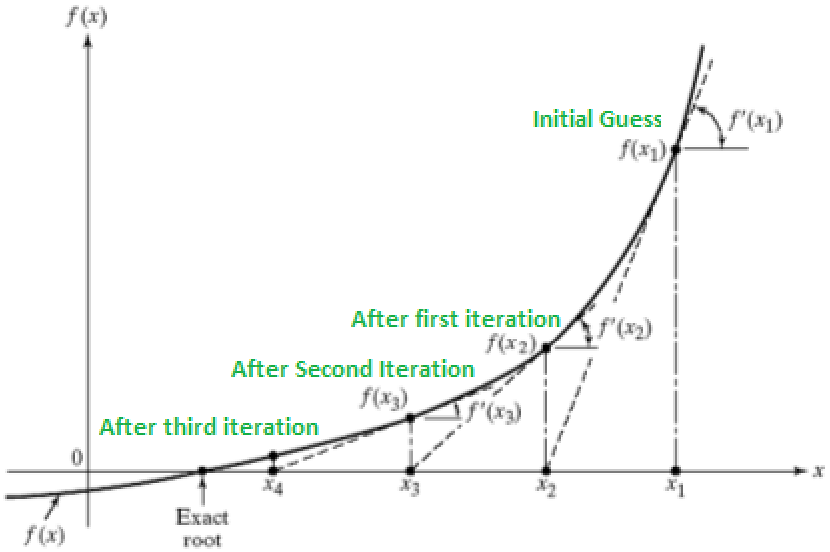
$$K_w = 10^{-14} \text{ M}$$

# Simple solution methods

Bisection method




Newton-Raphson method




https://en.wikipedia.org/wiki/Bisection_method
https://www.geeksforgeeks.org/program-for-newton-raphson-method/

# Parameter estimation

# Parameter estimation

- Also falls under the umbrella of optimization, operations research, data fitting, inverse modeling, etc.

- Purposes
  - model understanding (extract physical meaning from parameter values)
  - prediction / forecasting

- Estimate parameters for empirical, semi-empirical, and mechanistic models

- Example: chemical kinetic modeling [mechanistic, nonlinear], epidemiology [semi-empirical, linear], weather prediction [empirical, nonlinear]

# Example – reaction rate constants

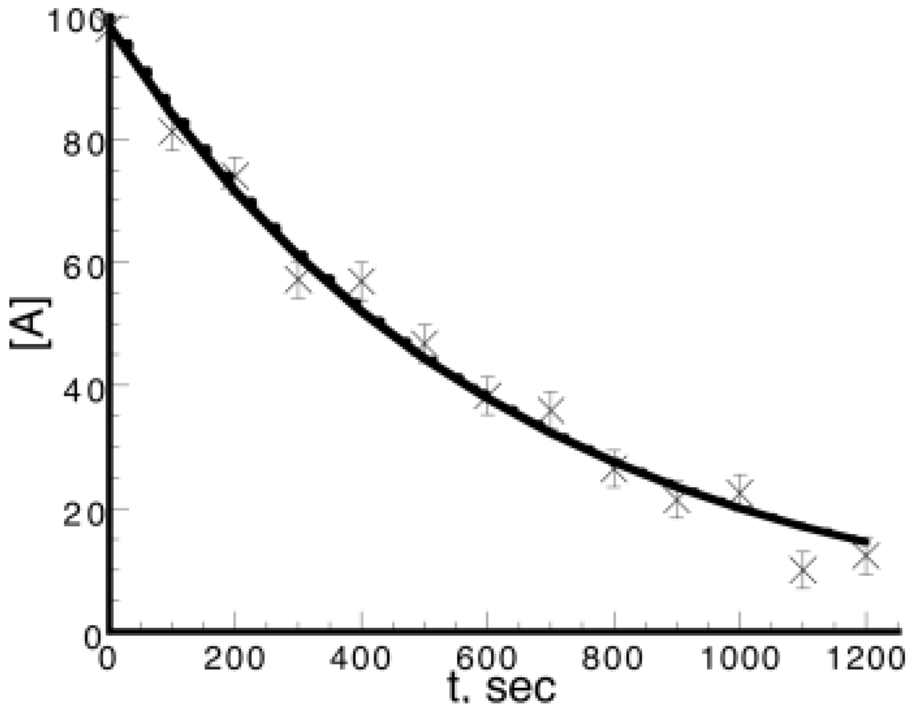
First order reaction

$$\mathrm{A} \xrightarrow{k} \mathrm{B}$$

$$v = \frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k[\mathrm{A}]$$

Solution to diff. eq. (estimate *k* to data)

$$[\mathrm{A}] = [\mathrm{A}]_0 \mathrm{e}^{-kt}$$

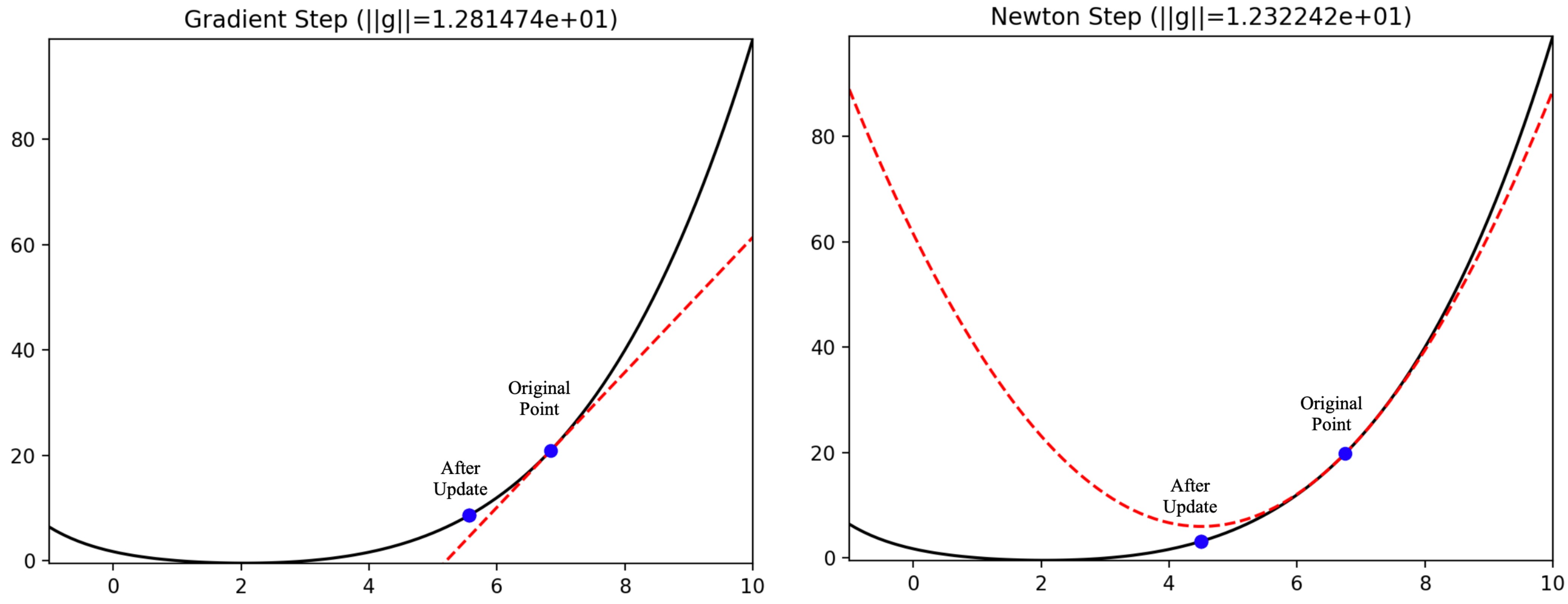



Objective / cost / loss function

$$J(k) = \arg\min_k \sum_i \{[\log([A]_0) - kt_i] - \log([A]_{\mathrm{obs},i})\}^2$$

Perrin, *J. Chem. Ed.*, 2017

# Some solution methods




https://www.cs.cornell.edu/courses/cs4780/2018fa/lectures/lecturenote07.html

Example of measurements used for deriving rate coefficients:

OH + $NO_2$ to products
$k = k(P,T)$

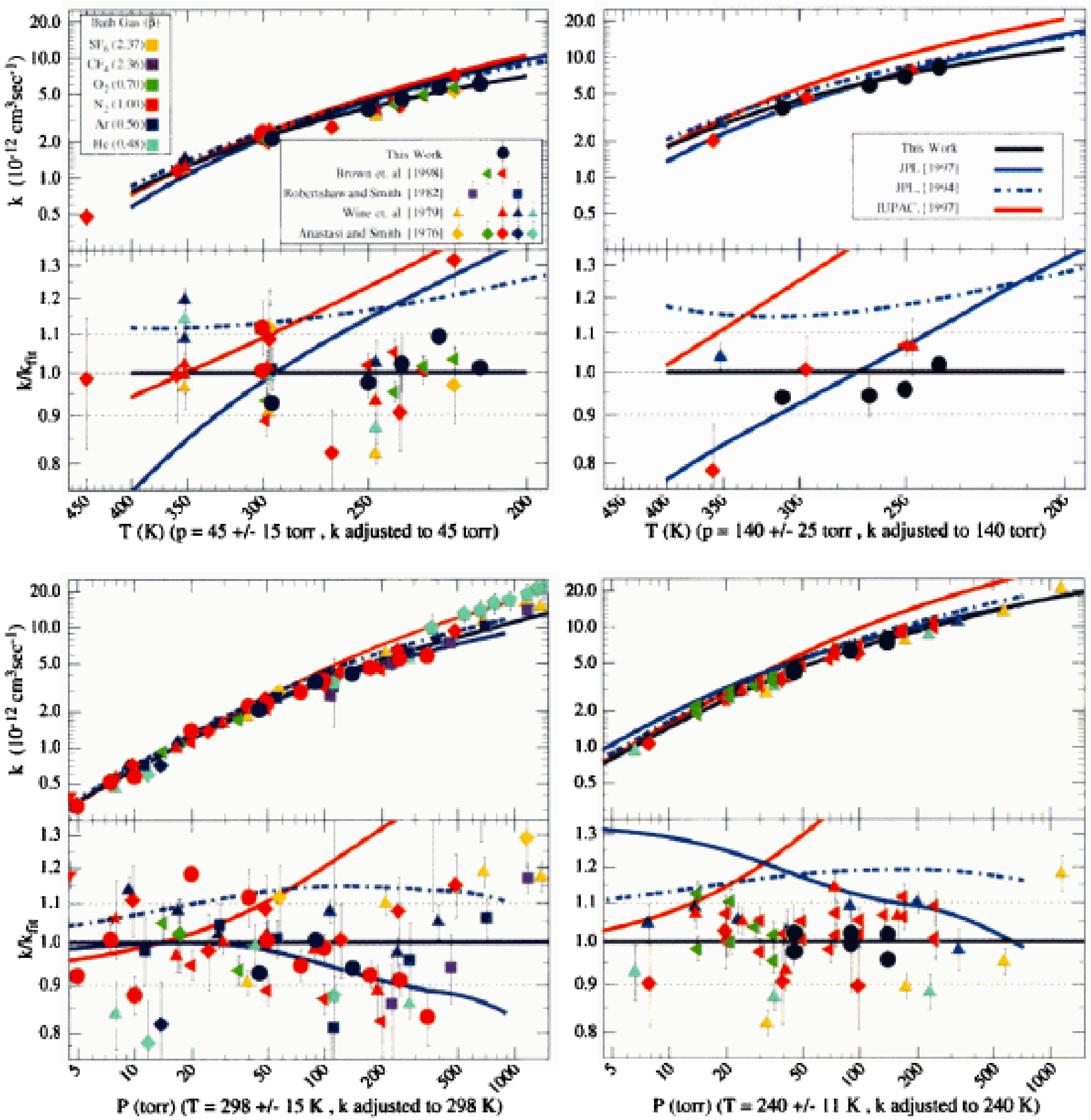



**Figure 1.** Data for the reaction OH + $NO_2$ → products as a function of pressure and temperature. Our data are plotted as solid black dots. Literature data are also shown, with different carrier gases represented by differing symbol colors. Symbol shapes identify the study responsible for each datum, as show in the legend; the red symbol color indicates nitrogen carrier gas (with the exception of our data, which are shown as solid black for emphasis). Pressures for bath gases other than $N_2$ are scaled by the collisional efficiency indicated in the legend. The latest IUPAC and JPL recommendations are shown as red and blue curves, while previous versions of these recommendations are shown as dashed curves of the same color. Our recommendation is shown as a black curve. The lower panel of each graph shows the ratio of each value to our recommendation.

Dransfield et al., *J. Geophys. Res.-Atmos.*, 1999

Parameters from various reactions are tabulated in a comprehensive database

JPL Publication 10-6

# Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies

## Evaluation Number 17

NASA Panel for Data Evaluation: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***National Institute of Standards and Technology***



**National Aeronautics and Space Administration**

**Jet Propulsion Laboratory**
**California Institute of Technology**
**Pasadena, California**

***June 10, 2011***


http://jpldataeval.jpl.nasa.gov/

**Table 2-1. Rate Constants for Termolecular Reactions**

| Reaction | Low-Pressure Limit[a] $k_0(T) = k_0^{300}(T/300)^{-n}$ | | High-Pressure Limit[b] $k_\infty(T) = k_\infty^{300}(T/300)^{-m}$ | | f | g | Notes |
|---|---|---|---|---|---|---|---|
| | $k_0^{300}$ | n | $k_\infty^{300}$ | m | | | |
| **$O_x$ Reactions** | | | | | | | |
| $O + O_2 \xrightarrow{M} O_3$ | (6.0) (–34) | 2.4 | – | – | 1.1 | 50 | A1 |
| **$O(^1D)$ Reactions** | | | | | | | |
| $O(^1D) + N_2 \xrightarrow{M} N_2O$ | (2.8) (–36) | 0.9 | – | – | 1.3 | 75 | A2 |
| **$HO_x$ Reactions** | | | | | | | |
| $H + O_2 \xrightarrow{M} HO_2$ | (4.4) (–32) | 1.3 | (7.5) (–11) | - 0.2 | 1.3 | 50 | B1 |
| $OH + OH \xrightarrow{M} H_2O_2$ | (6.9) (–31) | 1.0 | (2.6) (–11) | 0 | 1.5 | 100 | B2 |
| **$NO_x$ Reactions** | | | | | | | |
| $O + NO \xrightarrow{M} NO_2$ | (9.0) (–32) | 1.5 | (3.0) (–11) | 0.0 | 1.2 | 100 | C1 |
| $O + NO_2 \xrightarrow{M} NO_3$ | (2.5) (–31) | 1.8 | (2.2) (–11) | 0.7 | 1.3 | 100 | C2 |
| $OH + NO \xrightarrow{M} HONO$ | (7.0) (–31) | 2.6 | (3.6) (–11) | 0.1 | 1.2 | 50 | C3 |
| $OH + NO_2 \xrightarrow{M} HONO_2$ | (1.8) (–30) | 3.0 | (2.8) (–11) | 0 | 1.3 | 100 | C4 |
| $OH + NO_2 \xrightarrow{M} HOONO$ | (9.1) (–32) | 3.9 | (4.2) (–11) | 0.5 | 1.5 | 200 | C4 |
| $HO_2 + NO \xrightarrow{M} HONO_2$ | See Note | | | | | | C5 |
| $HO_2 + NO_2 \xrightarrow{M} HO_2NO_2$ | (2.0) (–31) | 3.4 | (2.9) (–12) | 1.1 | 1.1 | 50 | C6 |
| $NO_2 + NO_3 \xrightarrow{M} N_2O_5$ | (2.0) (–30) | 4.4 | (1.4) (–12) | 0.7 | 1.2 | 100 | C7 |
| $NO_3 \xrightarrow{M} NO + O_2$ | See Note | | | | | | C8 |

Formerly known as: *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*

## Chemical kinetic models are then integrated into chemical transport models which combine them with emissions, meteorology, and transport

The concentration of species $i$ is a function of space and time: $c_i = c_i(\mathbf{r}, t)$.

$$\frac{\partial c_i}{\partial t} = \left[\frac{\partial c_i}{\partial t}\right]_{\text{advection}} + \left[\frac{\partial c_i}{\partial t}\right]_{\text{dispersion}} + \left[\frac{\partial c_i}{\partial t}\right]_{\substack{\text{gas-phase}\\ \text{chemistry}}} + \left[\frac{\partial c_i}{\partial t}\right]_{\text{emission}} + \left[\frac{\partial c_i}{\partial t}\right]_{\substack{\text{wet/dry}\\ \text{deposition}}} + \left[\frac{\partial c_i}{\partial t}\right]_{\text{aerosol}} + \left[\frac{\partial c_i}{\partial t}\right]_{\substack{\text{aqueous-phase}\\ \text{chemistry}}}$$

Mass vs. number conservation for aerosols:

- mass is important for $PM_{2.5}$ and $PM_{10}$ regulation, light scattering, and mass budget considerations.
- number is important for simulating new particle formation and aerosol-cloud interactions.

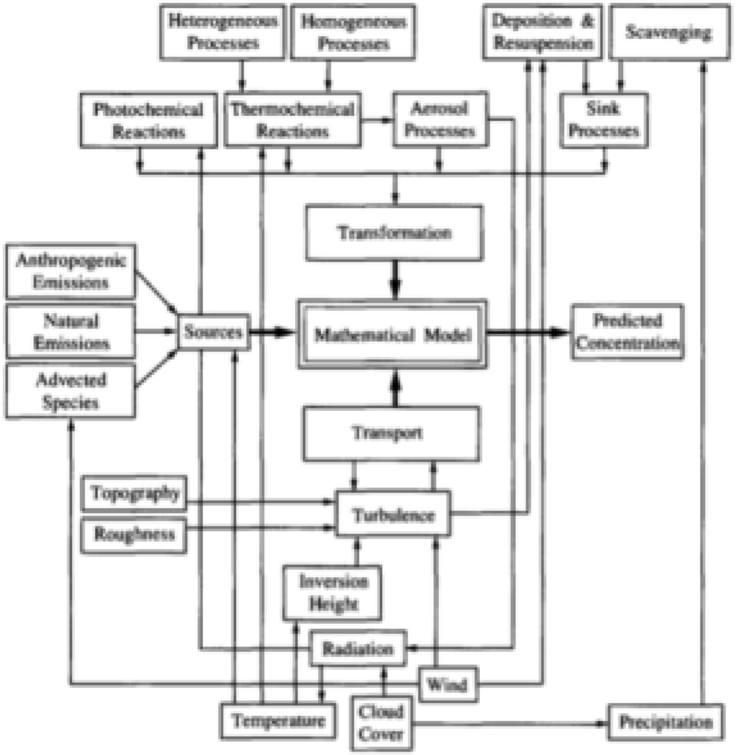



FIGURE 25.1 Elements of a mathematical atmospheric chemical transport model.

# Example: parameter estimation for epidemiology


ARTICLE

Check for updates

https://doi.org/10.1038/s41467-021-27484-1 OPEN

Secondary organic aerosol association with cardiorespiratory disease mortality in the United States

Havala O. T. Pye [1✉], Cavin K. Ward-Caviness [2], Ben N. Murphy [1], K. Wyat Appel[1] & Karl M. Seltzer [3]

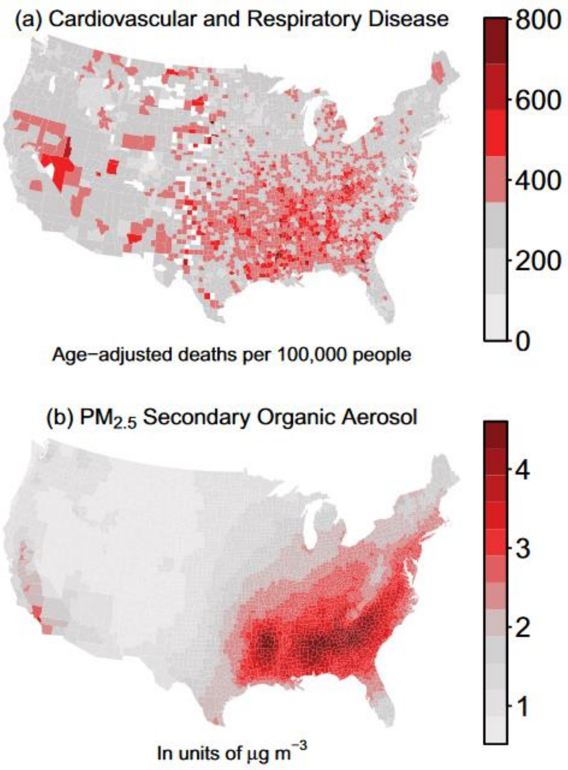
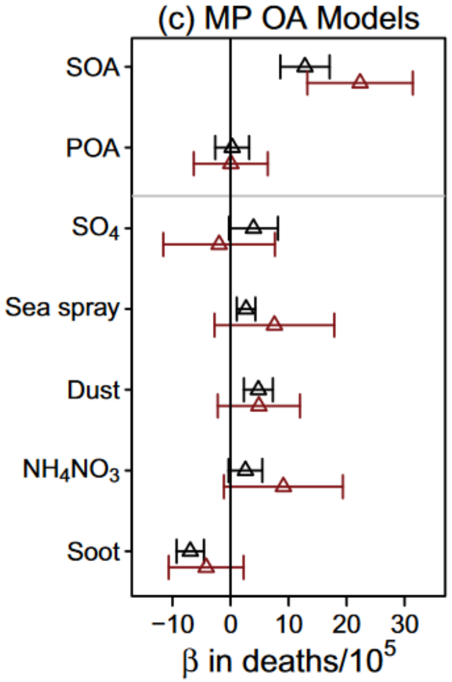


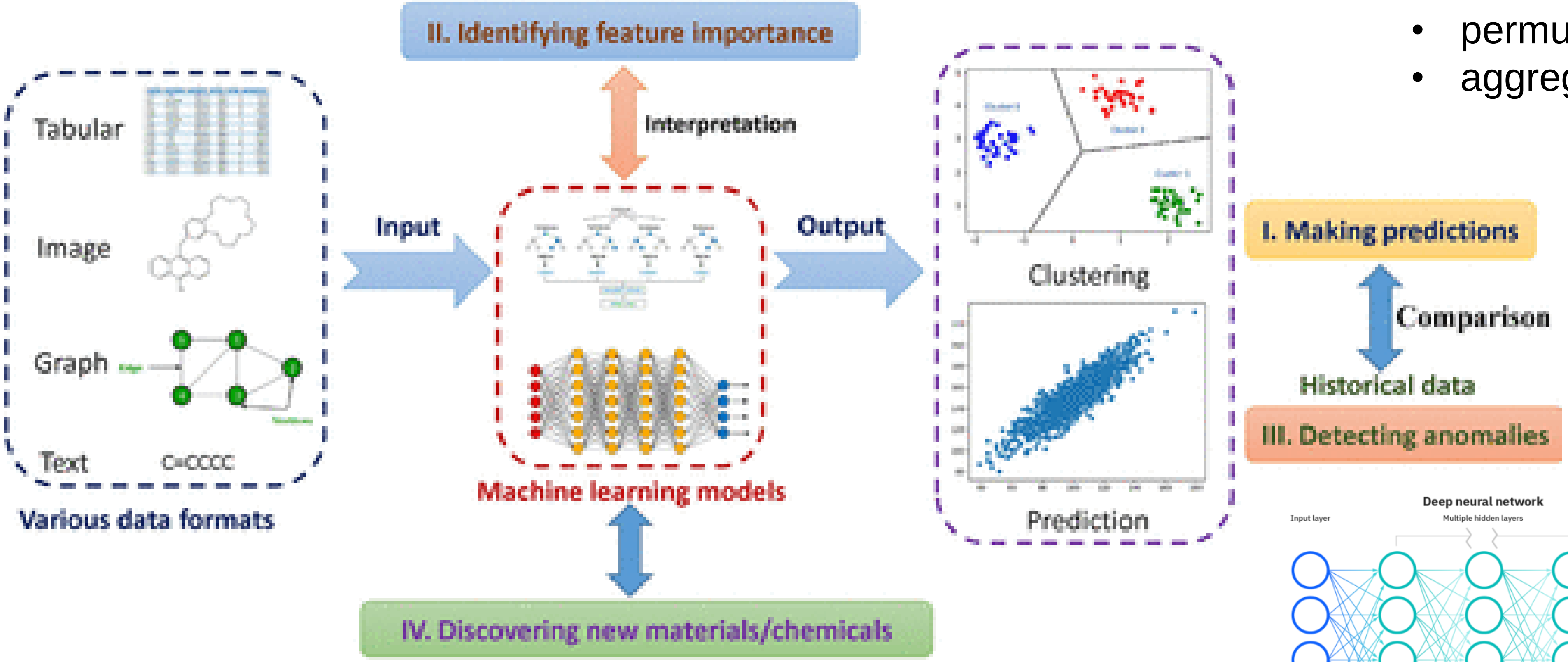

**Fig. 1 Cardiorespiratory disease mortality rates and secondary organic aerosol concentrations.** County-level, year 2016 (**a**) cardiovascular and respiratory disease age-adjusted death rates (per 100,000 in population) are from CDC and (**b**) $PM_{2.5}$ secondary organic aerosol concentrations are predicted by CMAQ. White in (**a**) indicates no death rate data while light gray indicates low reported rates.

$$
\begin{aligned}
\boldsymbol{D} = \beta_0 &+ \{\beta_1 \boldsymbol{PM}_{\boldsymbol{SOA_{BVOC}}} + \beta_2 \boldsymbol{PM}_{\boldsymbol{SOA_{AVOC}}} \\
&+ \beta_3 \boldsymbol{PM}_{\boldsymbol{POA}}\} + \beta_4 \boldsymbol{PM}_{\boldsymbol{Seaspray}} + \beta_5 \boldsymbol{PM}_{\boldsymbol{Soot}} \\
&+ \beta_6 \boldsymbol{PM}_{\boldsymbol{NH_4NO_3}} + \beta_7 \boldsymbol{PM}_{\boldsymbol{SO_4}} + \beta_8 \boldsymbol{PM}_{\boldsymbol{Dust}} + \sum_{j=1}^{N} \beta'_j \boldsymbol{C_j}
\end{aligned}
$$

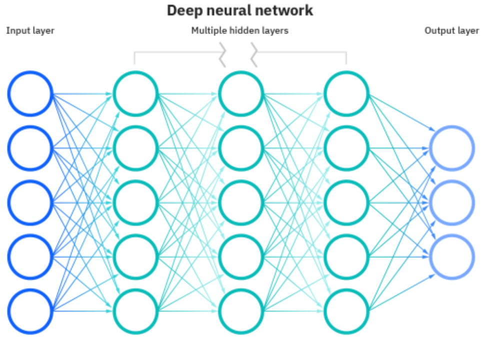


# Example: empirical models

Data preparation:
- cleaning
- curation
- permutation
- aggregation




Zhong et al., *ES&T*, 2021




$$\sum_{i=1}^{m} w_i x_i + bias = w_1 x_1 + w_2 x_2 + w_3 x_3 + bias$$

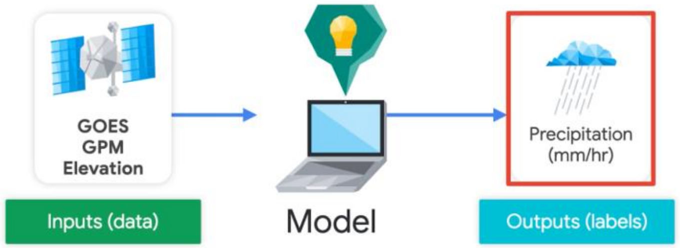
$$output = f(x) = \begin{cases} 1 \text{ if } \sum w_1 x_1 + b \geq 0 \\ 0 \text{ if } \sum w_1 x_1 + b < 0 \end{cases}$$

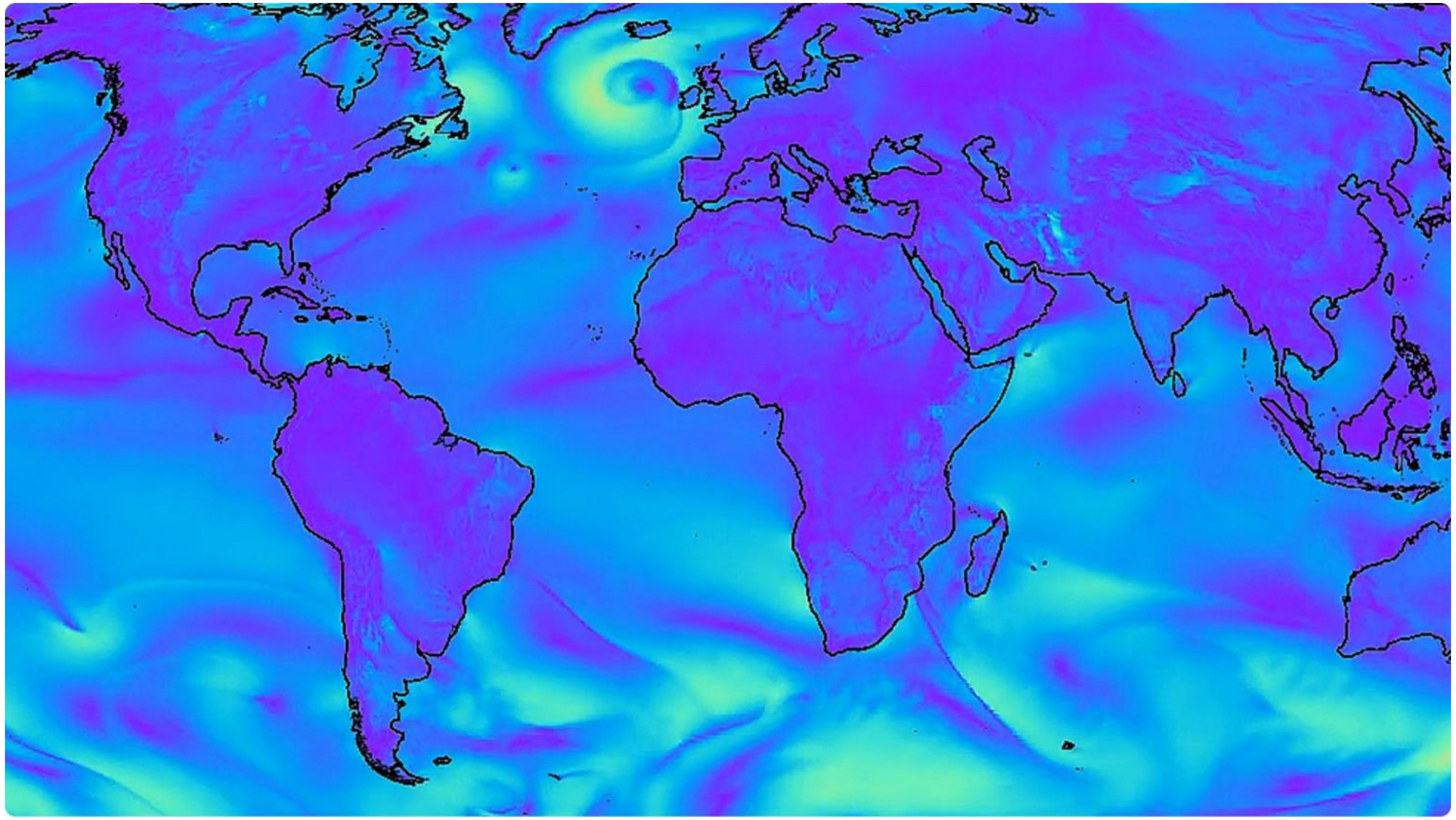
*https://www.ibm.com/cloud/learn/neural-networks*

GREGORY BARBER BUSINESS NOV 14, 2023 10:00 AM

# Google DeepMind's AI Weather Forecaster Handily Beats a Global Standard

Machine learning algorithms that digested decades of weather data were able to forecast 90 percent of atmospheric measures more accurately than Europe's top weather center.



https://cloud.google.com/blog/topics/sustainability/weather-prediction-with-ai
https://www.wired.com/story/google-deepmind-ai-weather-forecast/

# “Gotchas”

- Your estimated parameters may not be meaningful if your model (relationship among variables) is misspecified.

- Even if your model is “correct”, you may find solutions that represent local minima.

- Your predictions may not be meaningful if you are extrapolating outside of the domain of fitted data with an empirical function.

# Numerical integration

# Numerical integration

- Differential equation(s)
  - ODE: ordinary differential equation
  - PDE: partial differential equation

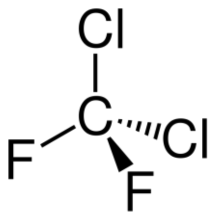
- Single, coupled, uncoupled

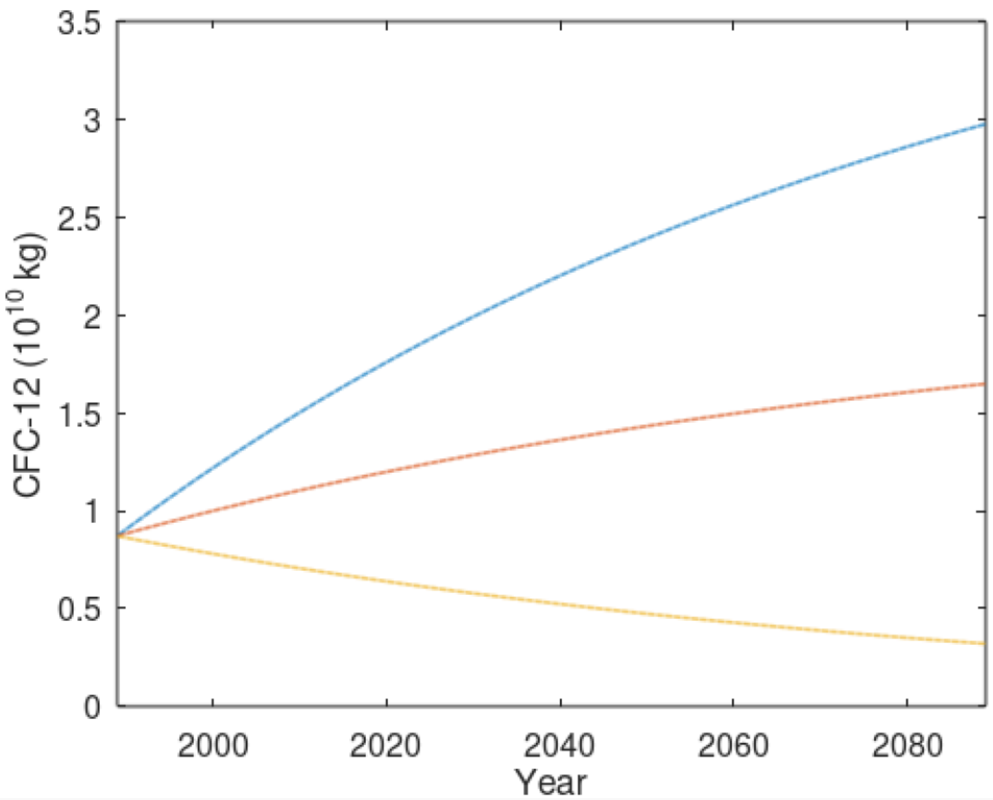
- Provide initial values / boundary values

- Examples: simulation of CFC-12 [single ODE], VOC-$NO_x$-$O_3$ system (urban smog) [coupled ODEs], 3D advection equation [PDE decoupled to independent ODEs]

# Example (ODE): simulation of dichlorofluoromethane

CFC-12






The mass balance for the photolysis of CFC-12 is given by:

$$\frac{dm}{dt} = E - k\,m$$

$m$ is the atmospheric mass of CFC-12, $E$ is the rate of emission, and $k$ is the rate of photolysis.

The atmospheric lifetime of CFC-12 is 100 years. Starting from an initial concentration of $m_0 = 400$ pptv in 1989, assume two scenarios:

"business as usual": E = $4.2 \times 10^8$ kg/yr

Scenario 1: base case (no change)

Scenario 2: 50% reduction in emissions

Scenario 3: 50% reduction in emissions before 1996
100% reductions afterward

Jacob, *Introduction to Atmospheric Chemistry*, 1999

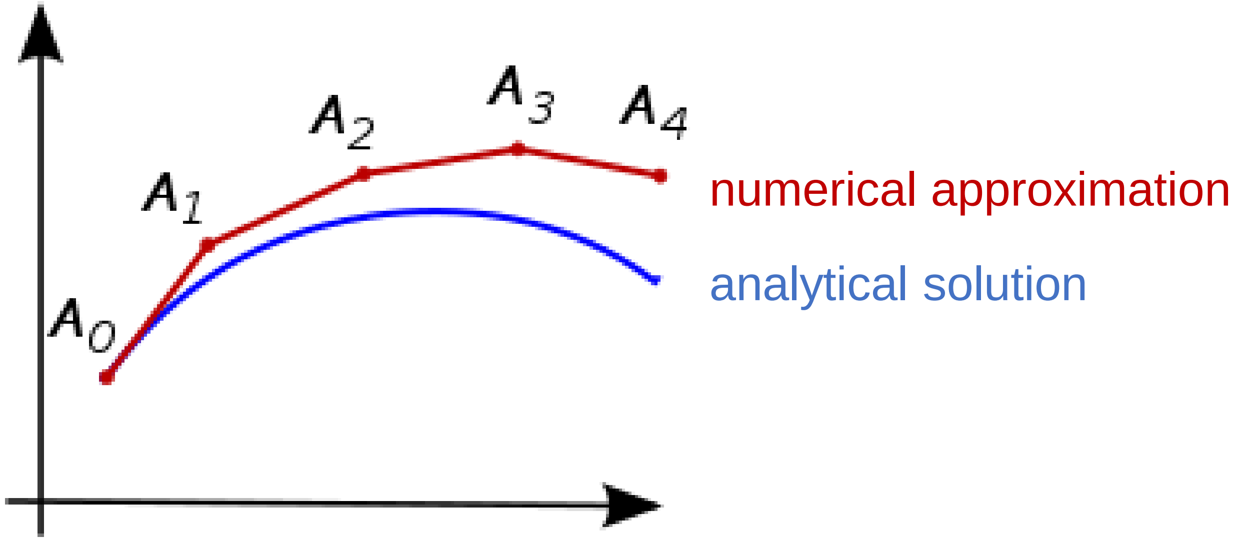
# Numerical integration

step size

Euler's method

$$y_{n+1} = y_n + hf(t_n, y_n)$$

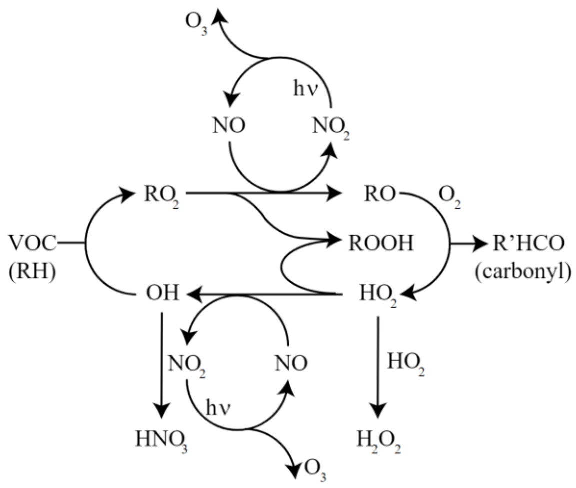
derivative




https://en.wikipedia.org/wiki/Euler_method

https://tutorial.math.lamar.edu/classes/de/eulersmethod.aspx

# Example (coupled ODEs): VOC-NO$_x$-O$_3$ system




$x$ = concentration

$\nu$ = stochiometric number

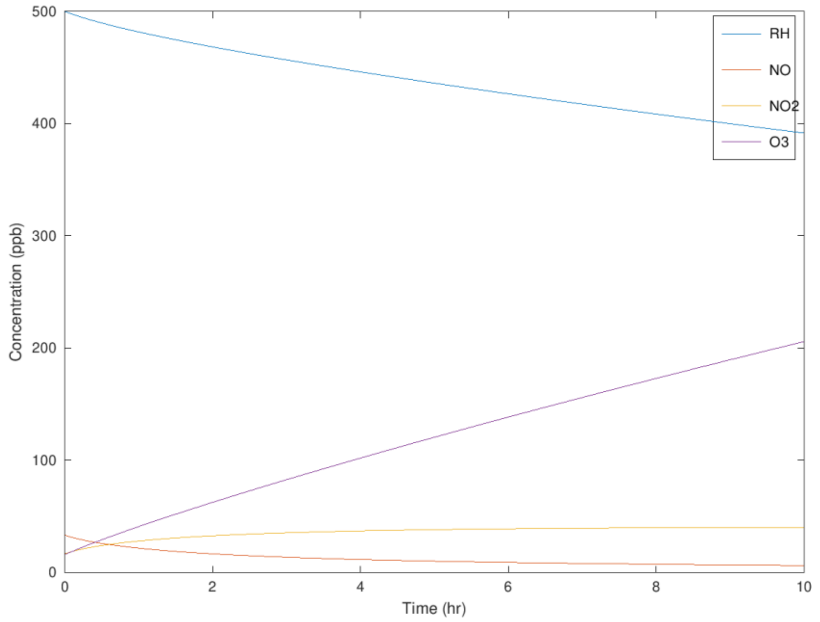
$r$ = reaction rate

$k$ = reaction rate constant

$$\frac{d\mathbf{x}}{dt} = \boldsymbol{\nu}\mathbf{r} = \boldsymbol{f}\left(\mathbf{x}, \mathbf{k}, \boldsymbol{\nu}\right), \quad \mathbf{x}(t=0) = \mathbf{x}_0$$

$$\frac{dx_i}{dt} = \sum_{j \,\in\, \text{reactions}} \nu_{ji} r_j, \text{ where } r_j = k_j \prod_{i \,\in\, \text{reactants}} x_i^{\nu_{ji}}$$

| | Reaction | Rate constant (298 K) |
|---|---|---|
| 1 | $RH + OH \xrightarrow{O_2} RO_2 + H_2O$ | $26.3 \times 10^{-12} cm^3\ molec^{-1}\ s^{-1}$ |
| 2 | $RO_2 + NO \xrightarrow{O_2} NO_2 + R'CHO + HO_2$ | $7.7 \times 10^{-12} cm^3\ molec^{-1}\ s^{-1}$ |
| 3 | $HO_2 + NO \rightarrow NO_2 + OH$ | $8.1 \times 10^{-12} cm^3\ molec^{-1}\ s^{-1}$ |
| 4 | $OH + NO_2 \xrightarrow{M} HNO_3$ | $1.1 \times 10^{-11} cm^3\ molec^{-1}\ s^{-1}$(at 1 atm) |
| 5 | $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ | $2.9 \times 10^{-12} cm^3\ molec^{-1}\ s^{-1}$ |
| 6 | $RO_2 + HO_2 \rightarrow ROOH + O_2$ | $5.2 \times 10^{-12} cm^3\ molec^{-1}\ s^{-1}$ |
| 7 | $NO_2 + h\nu \xrightarrow{O_2} NO + O_3$ | typical $\approx 0.015 s^{-1}$ |
| 8 | $O_3 + NO \rightarrow NO_2 + O_2$ | $1.9 \times 10^{-14} cm^3\ molec^{-1}\ s^{-1}$ |



# Numerical integration of PDEs

- Representation by operator splitting (requires small time steps)
- Discretization
- Finite difference
- Integration

Example: integrated modeling of multiple processes

# Processes

The concentration of species $i$ is a function of space and time: $c_i = c_i(\mathbf{r}, t)$.

$$\frac{\partial c_i}{\partial t} = \left[\frac{\partial c_i}{\partial t}\right]_{\text{advection}} + \left[\frac{\partial c_i}{\partial t}\right]_{\text{dispersion}} + \left[\frac{\partial c_i}{\partial t}\right]_{\text{gas-phase chemistry}} + \left[\frac{\partial c_i}{\partial t}\right]_{\text{emission}} + \left[\frac{\partial c_i}{\partial t}\right]_{\text{wet/dry deposition}} + \left[\frac{\partial c_i}{\partial t}\right]_{\text{aerosol}} + \left[\frac{\partial c_i}{\partial t}\right]_{\text{aqueous-phase chemistry}}$$

Mass vs. number conservation for aerosols:

- mass is important for $PM_{2.5}$ and $PM_{10}$ regulation, light scattering, and mass budget considerations.
- number is important for simulating new particle formation and aerosol-cloud interactions.

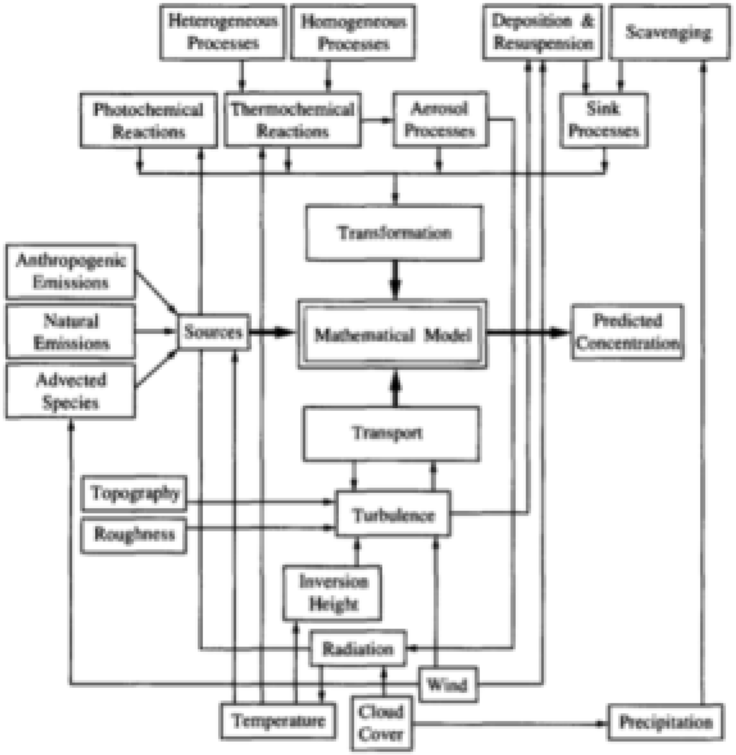



FIGURE 25.1 Elements of a mathematical atmospheric chemical transport model.

# Operator splitting

Let $\mathbf{c}(t) = c(\mathbf{r}, t)$. We can define an operator $X = X(\Delta t)$ and its corresponding incremental operator $\Delta X$:

$$X\,\mathbf{c}(t) = [\mathbf{c}(t + \Delta t)]_X \qquad = \mathbf{c}(t) + \int_t^{t+\Delta t} \left[\frac{\partial \mathbf{c}}{\partial \tau}\right] d\tau$$

$$\Delta X\,\mathbf{c}(t) = [\mathbf{c}(t + \Delta t) - \mathbf{c}(t)]_X = \int_t^{t+\Delta t} \left[\frac{\partial \mathbf{c}}{\partial \tau}\right] d\tau$$

Let $X$ represent various processes:

- $A$ Advection
- $D$ Diffusion
- $C$ Cloud
- $G$ Gas-phase chemistry
- $P$ Aerosol
- $S$ Source/sink

Operators can be applied in sequence or in parallel.

*Sequential operation*:

$$\mathbf{c}(t + \Delta t) = (S \circ P \circ G \circ C \circ D \circ A)\,\mathbf{c}(t)$$

where $\circ$ denotes operator composition: $f(g(x)) = (f \circ g)(x)$.

*Parallel operation*:

$$\mathbf{c}(t + \Delta t) = \mathbf{c}(t) + (\Delta S + \Delta P + \Delta G + \Delta C + \Delta D + \Delta A)\,\mathbf{c}(t)$$

# Example: advection equation

Operator splitting is also used to decouple the processes in space. Reverting back to representation of concentration as $c = c(\mathbf{r}, t)$, consider the advection equation:

$$\frac{\partial c}{\partial t} + \mathbf{u} \cdot \nabla c = 0$$

In Cartesion coordinates,

$$\frac{\partial c}{\partial t} = -u\frac{\partial c}{\partial x} - v\frac{\partial c}{\partial y} - w\frac{\partial c}{\partial x}$$

Applying the operators in parallel,

$$c(t + \Delta t) = c(t) + \left(\Delta A_x + \Delta A_y + \Delta A_z\right) c(t)$$

we can solve three one-dimensional equations instead of one three-dimensional equation:

$$\left[\frac{\partial c}{\partial t}\right]_x = -u\frac{\partial c}{\partial x}, \quad \left[\frac{\partial c}{\partial t}\right]_y = -v\frac{\partial c}{\partial y}, \quad \text{and} \quad \left[\frac{\partial c}{\partial t}\right]_z = -w\frac{\partial c}{\partial z}$$

**Discretization**. Discretizing the domain and defining the concentrations over this new domain,

$$c_{i,j,k}^{n} = c(x_i, y_j, z_k, t_n)$$
$$c_{i,j,k}^{n+1} = c(x_i, y_j, z_k, t_n + \Delta t)$$

**Representation by finite difference**. We can approximate with the simplest of (backward) finite difference approximations as

$$\frac{c_{i,j,k}^{n+1} - c_{i,j,k}^{n}}{\Delta t} = -\frac{u_{i,j,k}^{n} c_{i,j,k}^{n} - u_{i-1,j,k}^{n} c_{i-1,j,k}^{n}}{\Delta x}$$
$$\frac{c_{i,j,k}^{n+1} - c_{i,j,k}^{n}}{\Delta t} = -\frac{v_{i,j,k}^{n} c_{i,j,k}^{n} - v_{i,j-1,k}^{n} c_{i,j-1,k}^{n}}{\Delta y}$$
$$\frac{c_{i,j,k}^{n+1} - c_{i,j,k}^{n}}{\Delta t} = -\frac{w_{i,j,k}^{n} c_{i,j,k}^{n} - w_{i,j,k-1}^{n} c_{i,j,k-1}^{n}}{\Delta z}$$

**Integration** (by Euler's method). We get the solution with respect to advection as

$$c_{i,j,k}^{n+1} = c_{i,j,k}^{n} + \frac{u_{i-1,j,k}^{n} c_{i-1,j,k}^{n} - u_{i,j,k}^{n} c_{i,j,k}^{n}}{\Delta x}\Delta t + \frac{v_{i,j-1,k}^{n} c_{i,j-1,k}^{n} - v_{i,j,k}^{n} c_{i,j,k}^{n}}{\Delta y}\Delta t + \frac{w_{i,j,k-1}^{n} c_{i,j,k-1}^{n} - w_{i,j,k}^{n} c_{i,j,k}^{n}}{\Delta z}\Delta t$$

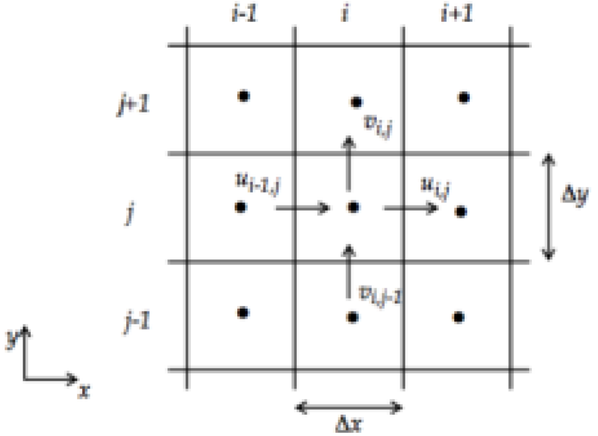
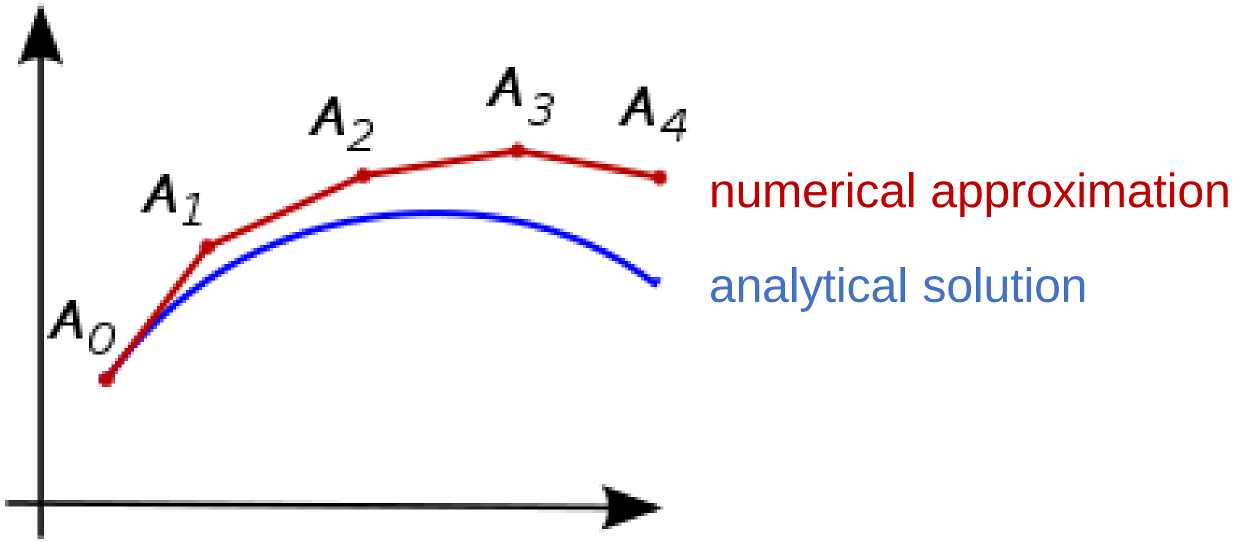



**Figure 5-2 Spatial discretization of the continuity equation (only two dimensions are shown). Dots indicate gridpoints at which the concentrations are calculated, and lines indicate gridbox boundaries at which the transport fluxes are calculated.**

Jacob, 1999

# “Gotchas”

- Your numerical approximation may not be meaningful if you pick the wrong (i.e., too large) step size (see stiff equations)
- Step size should be smaller than the timescale / spatial scale of phenomena your model describes



# For your project

- Many of these solvers, optimization algorithms, and numerical integration schemes are available in libraries.

- If other computational aspects of your project is high, then you can use these libraries.

- If other computation aspects of your project is low, then you can implement (i.e., code) your own version of these algorithms.

# Resources for further reading


- Chapra, Steven C. and Canale, Raymond P. *Numerical Methods for Engineers*, 8th ed. McGrall-Hill Education, 2021.

- Beer, Kenneth J. *Numerical Methods for Chemical Engineering: Applications in MATLAB*, Cambridge University Press, 2007.

- Ramaswami, Anu, Milford, Jana B., Small, Mitchell J. *Integrated Environmental Modeling: Pollutant Transport, Fate, and Risk in the Environment*. John Wiley & Sons, 2005.

- Jacob, Daniel. *Introduction to Atmospheric Chemistry*. Princeton University Press, 1999. Available online: http://acmg.seas.harvard.edu/people/faculty/djj/book/.

# Practical references for implementation

- https://ch.mathworks.com/help/symbolic/solve-equations-numerically.html

- https://ch.mathworks.com/discovery/data-fitting.html

- https://ch.mathworks.com/help/matlab/numerical-integration-and-differentiation.html