

Physics and Chemistry of Sustainability II

The Marvelous Side of Chemistry

Thermodynamics & Kinetics

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75 Years
of Free Thinking.

References

- ▶ G Job & R Rüffler: *Physical Chemistry from a Different Angle – Introducing Chemical Equilibrium, Kinetics and Electrochemistry by Numerous Experiments*, Springer, 2016 (English translation of the 1st German edition; 2nd German edition from 2021), DOI: 10.1007/978-3-319-15666-8
see also:
G Job & R Rüffler: *Physical Chemistry from a Different Angle Workbook – Exercises and Solutions*, Springer, 2019, DOI: 10.1007/978-3-030-28491-6
- ▶ DK Kondepudi & I Prigogine: *Modern Thermodynamics – From Heat Engines to Dissipative Structures*, 2nd ed., Wiley, 2015, DOI: 10.1002/9781118698723
- ▶ JD Seader, EJ Henley & DK Roper: *Separation Process Principles – Chemical and Biochemical Operations*, 3rd ed., Wiley, 2011
- ▶ Additional references as indicated

Thermodynamics

(only Phenomenological Thermodynamics, not Statistical Thermodynamics)

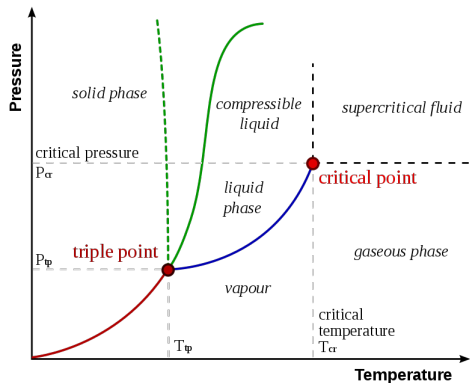
Thermodynamics

(Only) Three types of thermodynamic systems exist:

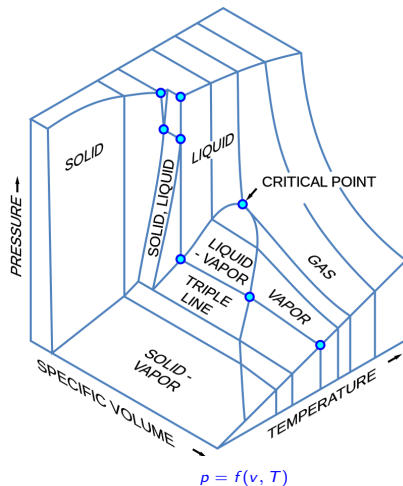
- ▶ **Isolated systems:** neither matter nor energy can be exchanged with the environment, the system's entropy increases until it reaches a maximum
Examples: the entire universe, certain lab apparatuses (only approximately)
- ▶ **Closed systems:** energy (e. g. heat, light), but not matter, can be exchanged with the environment, entropy of system and environment together increases
Examples: our planet Earth (in good approximation), certain lab apparatuses
- ▶ **Open systems:** both matter and energy can be exchanged with the environment, entropy of system and environment together increases
Examples: all living organisms (bacteria, fungi, plants, animals, you & me), a building, a village, a town, a county, a country, a continent, certain lab apparatuses
- ▶ An exchange of matter only, without exchange of energy, is not possible,
 - (i) because moving/flowing matter has kinetic energy and
 - (ii) because matter at $T > 0$ K contains thermal energy (latent heat)

Thermodynamics

Phase diagram for a single pure simple compound



red: sublimation curve (solid \rightleftharpoons gas)
green: melting curve (solid \rightleftharpoons liquid)
blue: boiling curve (liquid \rightleftharpoons gas)



https://en.wikipedia.org/wiki/Phase_diagram (accessed 14 May 2024)

Thermodynamics

Gibbs' phase rule (1870s): If F is the number of degrees of freedom, C the number of components and P the number of phases, then

$$F = C - P + 2$$

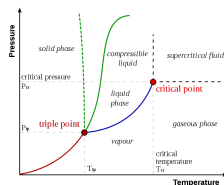
Proof: F is the difference between the number of variables $(C - 1)P + 2$ * and the number of constraints $C(P - 1)$ **

$$F = (C - 1)P + 2 - C(P - 1) = C - P + 2$$

* The expression $(C - 1)P + 2$ counts, for every phase, the variables for chemical composition (given, e.g., by mole fractions x_k , $k = 1, \dots, C$, including one constraint, which is $\sum_k x_k = 1$ in case that mole fractions are used) and, finally, adds two more variables, these latter typically being pressure p and temperature T for chemical applications.

** The expression $C(P - 1)$ counts, for every compound k , $k = 1, \dots, C$, the conditions of equality of chemical potential μ_k between different phases (this term does not contribute if just a single phase exists, i.e. when $P = 1$).

Phase diagram



Gibbs' phase rule

- Number of independently selectable parameters F (= degrees of freedom)

$$F = C - P + 2$$

F : Degrees of freedom, C : Number of components, P : Number of phases

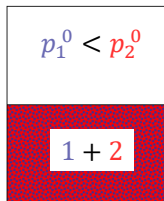
- **Example 1:** Pure compound (e.g. water) one phase (e.g. liquid): $F = 2$
→ Temperature and pressure can be chosen independently (in phase range)
- **Example 2:** Water at boiling point curve ($P = 2$): $F = 1$
→ Temperature depends on pressure (or vice versa)

Phase diagram – multiple components

- Ideal binary mixture (molecular interactions same as pure components)

x_1 : Mole fraction of component 1 in liquid mixture ($x_2 = 1 - x_1$)

y_1 : Mole fraction of component 1 in vapor mixture ($y_2 = 1 - y_1$)



p_1^0 : Vapor pressure of pure component 1 (equilibrium)

p_2^0 : Vapor pressure of pure component 2 (equilibrium)

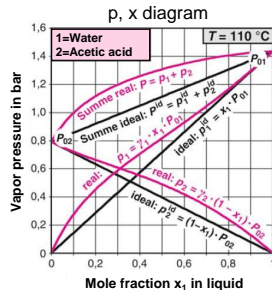
Raoult's + Dalton's law

$$p = p_1^0 x_1 + p_2^0 x_2$$

- Total vapour pressure of an ideal mixture of liquids is equal to the sum of vapor pressures of the pure components multiplied by its mole fraction in the mixture

Phase diagram – multiple components

- Ideal vs. real mixtures



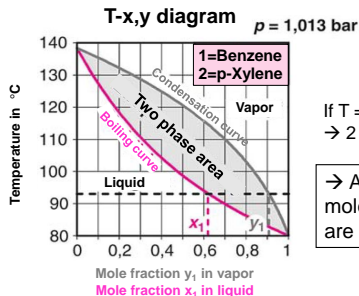
Phase diagram – multiple components

Gibbs' phase rule: $F = C - P + 2$

- **Example 3:** Benzene-xylene mix ($C = 2$) $\rightarrow F = 4 - P$

Thermodynamic variables:

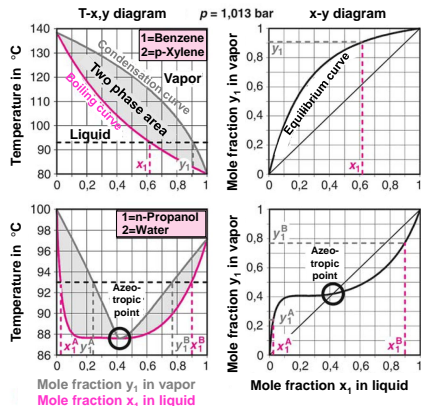
1. Temperature (T)
 2. Pressure (p)
 3. Mole fraction of benzene in liquid phase (x_1)
 4. Mole fraction of benzene in vapour phase (y_1)
- (3. & 4. may also be xylene, dependent variables)



If $T = 80 - 140 \text{ }^\circ\text{C}$
 $\rightarrow 2 \text{ phases} \rightarrow \underline{F = 2}$

\rightarrow At given T & p,
 mole fractions
 are defined

Phase diagram – multiple components



Thermodynamics

Thermodynamic square (Born square, Guggenheim scheme):*

Connecting thermodynamic potentials A (or F), G , H , U and state variables V , S (extensive) and p , T (intensive), such that (see refs. for details):

$$U = U(S, V) \Rightarrow dU = T dS - p dV$$

$$H = H(S, p) \Rightarrow dH = T dS + V dp$$

$$G = G(T, p) \Rightarrow dG = -S dT + V dp$$

$$A = A(T, V) \Rightarrow dA = -S dT - p dV$$

For multicomponent systems add, for every compound k , a term with chemical potential μ_k and particle number N_k , e.g.

$$dG = -S dT + V dp + \sum_k^C \mu_k dN_k$$

(to be considered for every phase in the system)

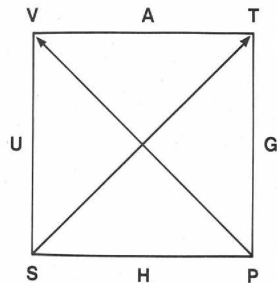


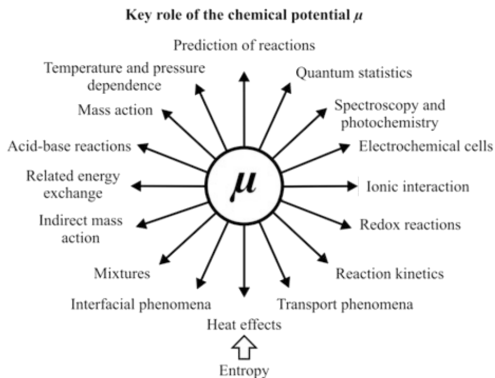
Figure 1. Thermodynamic square.

For Chemistry (constant T , p), we thus arrive at

$$dG = \sum_k^C \mu_k dN_k$$

At chemical equilibrium, $dN_k = 0$ for all k
 $\leadsto dG = 0$, i.e. Gibbs free energy is stationary

* after M Born (1882–1970, 1954 Nobel Prize in Physics) and EA Guggenheim (1901–1970)
A mnemonic in English: **Good Physicochemists have studied under very ambitious (fine) teachers**
https://en.wikipedia.org/wiki/Thermodynamic_square, <https://de.wikipedia.org/wiki/Guggenheim-Quadrat>
RF Fox, J Chem Educ **53** (1976) 441, <https://doi.org/10.1021/ed053p441>



Because we choose in this book an approach to matter dynamics directly by using the chemical potential, application of the concept of entropy is limited to the description of heat effects. Still, entropy retains its fundamental importance for this subject and is correspondingly discussed in detail.

Chemical potential μ and entropy S — the essential central thermodynamic quantities

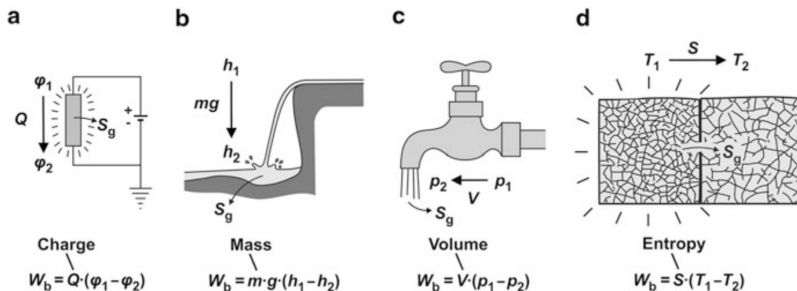


Fig. 3.36 Energy release and entropy generation for (a) a potential drop of charge, (b) a mass falling from a height, (c) a pressure drop of a volume, (d) a temperature drop of entropy.

G Job, R Ruffler: Physical Chemistry from a Different Angle, Springer, 2016, p 90

Thermodynamics

- ▶ 1931 – L Onsager (USA, 1968 Nobel Prize in Chemistry): Thermodynamics of irreversible processes “not far from equilibrium” (or: *linear* non-equilibrium thermodynamics)

Entropy production P inside the system can be described as a sum of products of fluxes J_k caused (induced) by conjugated generalized forces X_k :

$$P = \frac{dS_{\text{int}}}{dt} = \sum_{k=1}^n J_k X_k \geq 0$$

In the “linear regime”, fluxes J_k are expected to depend linearly on forces X_ℓ , e.g.

$$\left. \begin{aligned} J_1 &= L_{11}X_1 + L_{12}X_2 \\ J_2 &= L_{21}X_1 + L_{22}X_2 \end{aligned} \right\} \Leftrightarrow \underline{J} = \begin{pmatrix} J_1 \\ J_2 \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \end{pmatrix} = \underline{\underline{L}} \underline{X}$$

Onsager reciprocal relations: $L_{k\ell} = L_{\ell k}$ ($k \neq \ell$), $\underline{\underline{L}} = \underline{\underline{L}}^T$ ($\underline{\underline{L}}$ is a symmetric matrix)
Example: Coefficients in the theory of thermoelectric effects (Peltier, Seebeck)

Thermodynamics

Some examples for “fluxes” depending linearly on “generalized forces”:

Table 1. Linear Relations between Disequilibrium Degrees and Flows for Some Irreversible Processes

Process	Law	Flow	Disequilibrium Degree	Phenomenological Coefficient
Electrical conduction	$I = V/R$	I	V	$1/R$
Chemical diffusion	$J_k = -D_k(dC_k/dx)$	J_k	dC_k/dx	$-D_k$
Heat conduction	$J_q = -\kappa(dT/dx)$	J_q	dT/dx	$-\kappa$
Chemical reaction	$J = -L \Delta G$	J	ΔG	$-L$

JChemEd.chem.wisc.edu • [Vol. 79 No. 11 November 2002](https://doi.org/10.1021/ed079p1336) • [Journal of Chemical Education](https://doi.org/10.1021/ed079p1336) **1337**

The first three examples in the table are, from top to bottom, Ohm's law (essentially), 1st Fick's law and Fourier's law.

JC Aledo, A Esteban del Valle: Glycolysis in Wonderland: The Importance of Energy Dissipation in Metabolic Pathways, J Chem Educ **79** (2002) 1336
<https://doi.org/10.1021/ed079p1336>

Thermodynamics

- ▶ Internal entropy production “not far from equilibrium” is thus, in general, a quadratic function (paraboloid) of the generalized forces, X_k ,

$$P = \frac{dS_{\text{int}}}{dt} = \sum_{k=1}^n J_k X_k = \underline{X}^T \underline{L} \underline{X}$$

which has a minimum

→ Principle of Minimal Entropy Production (Prigogine, 1940s)

- ▶ 1940s/1950s – I Prigogine (Belgium, 1977 Nobel Prize in Chemistry): Thermodynamics of systems “far away from equilibrium” (or: *non-linear* non-equilibrium thermodynamics); dissipative structures generated by flow of matter/energy into/through/out of open systems
Examples: Bénard cells (convective heat transport in viscous fluids), living cells
- ▶ 1960s/1970s – M Eigen (Germany, 1967 Nobel Prize in Chemistry): Theory of hypercycles (describing selforganization in prebiotic systems)

Thermodynamics

Table 5. *Definitions and relations of chemical thermodynamics*

Affinity of reaction i :

$$A_i = - \sum_k \nu_{ik} \mu_k, \quad (1)$$

$$= R T \left[\ln K_i - \ln \prod_k a_k^{\nu_{ik}} \right]. \quad (2)$$

Stoichiometric coefficients:

$$\nu_{ik} \begin{cases} > 0 & \text{for reaction products} \\ < 0 & \text{for reactants.} \end{cases}$$

Example: $4 \text{O}_2 + \text{Hb} \rightleftharpoons \text{Hb}(\text{O}_2)_4$:

$$\nu_{\text{O}_2} = -4; \quad \nu_{\text{Hb}} = -1; \quad \nu_{\text{Hb}(\text{O}_2)_4} = +1;$$

Chemical potential of substance k :

$$\mu_k = \mu_k^0 + R T \ln a_k \quad (3)$$

μ_k^0 = standard chemical potential; a_k = activity (to be replaced by concentration c_k for ideal solutions).

Equilibrium constant:

$$K_i = \prod_k \bar{a}_k^{\nu_{ik}} \quad (4)$$

\bar{a}_k refers to equilibrium state, where $A_i \equiv 0$;

$$- R T \ln K_i = \sum_k \nu_{ik} \mu_k^0 \quad (\text{cf. Eq. (2)}). \quad (5)$$

Extent of reaction ξ_i according to:

$$d\xi_i = dn_k / \nu_{ik} \quad (n_k = \text{mole number of component } k). \quad (6)$$

At const T and P :

$$dG = \sum_i A_i d\xi_i \quad (7)$$

(G = Gibbs' free energy; ξ_i is conjugate to A_i).

Reaction Rate:

$$V_i = d\xi_i/dt = \sum_k \varepsilon_{ik} \cdot A_k/T \quad (8)$$

(ε_{ik} = phenomenological coefficients).

Onsager's Relations:

$$\varepsilon_{ik} = \varepsilon_{ki}. \quad (9)$$

Linearization:

$$V_i = \frac{1}{T} \sum_k \varepsilon_{ik} \sum_l (\partial A_k / \partial \xi_l)_{T,P} \delta \xi_l. \quad (10)$$

The matrix (ε_{ik}) and the tensor $(\partial A_k / \partial \xi_l)_{T,P}$ can be written in diagonal form. The transformed rate equations assume the form:

$$V_i' = d\xi_i'/dt = \lambda_i \delta \xi_i', \quad (11)$$

where $\delta \xi_i'$ = normal mode;

$\lambda_i = -1/\tau_i$ = eigenvalue; τ_i = relaxation time;

the solution of the rate equation is

$$\delta \xi_i' = \delta \xi_{i0}' e^{-t/\tau_i}. \quad (12)$$

Entropy production:

$$\sigma = \frac{1}{T^2} \sum_{ik} \varepsilon_{ik} A_i A_k \geq 0. \quad (13)$$

The essence of entropy production can be illustrated by glycolysis.^[14] Anaerobic glycolysis is an ATP-producing process in living organisms. Endergonic ATP production from ADP is coupled to exergonic transformation of glucose to lactate. The energy produced in the reaction of one molecule of glucose is sufficient for the formation of four molecules of ATP. Still only half of that energy is used for that purpose, and thus merely two molecules of ATP produced, the rest is dissipated as heat. The dissipated energy promotes a high disequilibrium degree, and is essential for driving the flow of matter throughout the glycolytic pathway, thereby avoiding chemical equilibrium.^[14]

C Moberg: Schrödinger's *What is Life?* — The 75th Anniversary of a Book that Inspired Biology, *Angew Chem Int Ed* **59** (2020) 2550
<https://doi.org/10.1002/anie.201911112>
JC Aledo, A Esteban del Valle, *J Chem Educ* **79** (2002) 1336, <https://doi.org/10.1021/ed079p1336>

Thermodynamics

General expression for entropy production in a system (volume V , surface area Σ):

$$\frac{dS}{dt} = \frac{dS_{\text{ext}}}{dt} + \frac{dS_{\text{int}}}{dt} \geq 0$$

with entropy transported per unit time through the surface area Σ of the system by entropy current density $\underline{j}_S(\underline{r}, t)$ ($d\underline{f}$ outward-pointing vector of a differential surface area element)

$$\frac{dS_{\text{ext}}}{dt} = - \int_{\Sigma} \underline{j}_S(\underline{r}, t) \cdot d\underline{f}$$

and entropy produced per unit time within the volume V of the system by entropy production density $\sigma_S(\underline{r}, t)$ ($d\tau$ differential volume element)

$$\frac{dS_{\text{int}}}{dt} = + \int_V \sigma_S(\underline{r}, t) d\tau$$

R Kümmel: The Impact of Entropy Production and Emission Mitigation on Economic Growth, Entropy **18** (2016) 75,
<https://doi.org/10.3390/e18030075>

R Kümmel, The Second Law of Economics — Energy, Entropy, and the Origins of Wealth, Springer, 2011,
<https://doi.org/10.1007/978-1-4419-9365-6>

Thermodynamics & Economy (1929) — Did we learn it?

THERMODYNAMIK

DIE LEHRE VON DEN KREISPROZESSEN
DEN PHYSIKALISCHEN UND CHEMISCHEN
VERÄNDERUNGEN UND GLEICHGEWICHTEN

EINE HINZFÜHRUNG ZU DEN THERMODYNAMISCHEN PROBLEMEN
UNSERER KRAFT- UND STOFFWIRTSCHAFT

VON

DR. W. SCHOTTKY

WISSENSCHAFTLICHEM BERATER DER SIEMENS & HALSKE A.-G.
FRÜHER ORIENTLICHEM PROFESSOR FÜR THEORETISCHE PHYSIK
AN DER UNIVERSITÄT ROSTOCK

IN GEMEINSCHAFT MIT

DR. H. ULICH UND DR. C. WAGNER
PRIVATDOZENT UND ASSISTENT FÜR PHYSIKALISCHE CHEMIE
AN DER UNIVERSITÄT ROSTOCK

PRIVATDOZENT UND ASSISTENT
AM CHEMISCHEN LABORATORIUM
DER UNIVERSITÄT JENA

MIT 90 ABBILDUNGEN UND 1 TAFEL



BERLIN
VERLAG VON JULIUS SPRINGER
1929

English translation of 1st sentence of preface:

The time of unhesitating economic activity using the energy and material sources provided to us by nature will probably have only the meaning of a bygone economic era already for our children.

W Schottky, H Ulich, C Wagner: Thermodynamik, Springer, 1929, Reprint 1973, <https://link.springer.com/book/10.1007/978-3-642-99060-1>
(preface freely accessible)

Vorwort.

Die Zeit des unbedenklichen Wirtschaftens mit den Energiequellen und Stofflagern, die uns die Natur zur Verfügung gestellt hat, wird wahrscheinlich schon für unsere Kinder nur noch die Bedeutung einer vergangenen Wirtschaftsepoche haben. Daß die Optimisten recht behalten, die auf die Erschließung ungeahnter neuer Wege zur Energiegewinnung und Stoffumwandlung hoffen, wollen wir wünschen; als vorsichtige Wirte stehen wir aber vor der Aufgabe, uns heute auf lange Sicht mit den vorhandenen Mitteln einzurichten: mit unserem Einkommen, bestehend aus den unveränderlich fließenden Energiequellen, vor allem den Wasserkraften, und mit unserem Vermögen, den Kohle- und Öllagern und den hochwertigen Rohprodukten.

Kostbare Rohstoffe kann man, wir haben es erfahren, für fast jeden Verwendungszweck durch ein als Rohstoff mehr oder weniger wertloses Material ersetzen: Energie ist unersetzbar. Arbeitsfähige Energie ist absolutes Gut, ist absoluter volkswirtschaftlicher Reichtum; sie vermag nicht nur unsere Lasten zu heben, unsere mechanischen Arbeiten zu verrichten, unsere Fahrzeuge zu bewegen, sie schafft uns auch auswertlos, überall vorhandener Substanz begehrteste Edelstoffe und höchstwertige Verbindungen. Der potentielle Reichtum eines Landes, die landwirtschaftlichen Produktionsmöglichkeiten in gewissem Sinne eingeschlossen, hängt heute fast ausschließlich von der ihm zur Verfügung stehenden freien, arbeitsfähigen Energie ab.

Denken wir uns diesen ganzen potentiellen Reichtum erschlossen, alle Wasserkräfte ausgebaut, die Kohlen- und Öllager in einem vernünftigen Tempo ausgewertet. Dann steht aber vor dem dadurch gegebenen Brutto-Wohlstand immer noch ein Faktor, der erst den wirklichen, den effektiven Reichtum bestimmt: der Wirkungsgrad der freien Energie, der in der Ausnutzung von Brennstoffen zur Erzeugung mechanischer Arbeit, in der Ausnutzung der Energiequellen zur Erzeugung hochwertiger Stoffe und Verbindungen errichtet wird. Eine Erhöhung dieses Wirkungsgradfaktors um 10% steigert die wirtschaftlichen Hilfsmittel jedes Bürgers um 10%. Er stellt eine Intelligenzprämie dar, die die Natur uns gewährt.

„Intelligenzprämie“ ist natürlich nicht ganz richtig. Damit ein Volk von den ihm verliehenen energetischen Hilfsmitteln den sächlich günstigsten Gebrauch macht, muß zunächst eine Reihe von rein menschlichen und sozialen Voraussetzungen erfüllt sein; und unendlich viele glückliche Einfälle im großen und kleinen, viel intuitive Hingabe an rein handwerkliche und fabrikatorische Probleme und vor allem noch eine Unsumme intensiver Arbeit wird nötig sein, ehe das Schwergewicht der weiteren Entwicklung auf die rein geistige Seite verlegt ist.

Immerhin befinden wir uns heute schon auf dem Wege zu einer solchen Entwicklung, und so spielt die intellektuelle Komponente, die rechnerische Vorabklärung zu erwartender Effekte auf gegebener Grundlage oder das Aufsuchen der optimalen Bedingungen einer gestellten technischen Aufgabe, bei

1*

Kinetics

The Language of Change

For countable/measurable stuff:

Q: How to describe changes of amount of that stuff over time? How to describe changes/differences in space (in position)?

A: Set up and (try to) solve differential equations!

Ordinary Differential Equations (ODEs)
for $f(x)$ or $f(t)$

Partial Differential Equations (PDEs)
for $f(\underline{x})$ or $f(\underline{x}, t)$



Astérix: Le Domaine des Dieux (English: The Mansions of the Gods, 1973; German: Die Trabantentstadt, 1974), comic book series, vol. 17, p. 15

People think that
mathematics is
complicated. Mathematics
is the simple bit, it's the
stuff we CAN understand.
It's cats that are
complicated.

John Horton Conway

WWW.STOREMYPIC.COM



John H. Conway (1937–2020), known for “Conway’s Game of Life” (1968)

Picture: R. T. Curtis, *Biographical Memoirs of Fellows of the Royal Society* **72** (2022) 117, DOI:10.1098/rsbm.2021.0034
https://en.wikipedia.org/wiki/Cellular_automaton

Some simple (and naïve) growth laws

- ▶ **Exponential growth/decay** (k growth/decay constant, SI unit $[k] = s^{-1}$):
Differential equation:

$$\dot{Q} = \frac{dQ}{dt} = k Q$$

$$\dot{Q} - k Q = 0$$

Integrated forms:

$$Q(t) = Q_0 \exp [k(t - t_0)] \quad (Q_0 = Q(t_0))$$

– linearized:

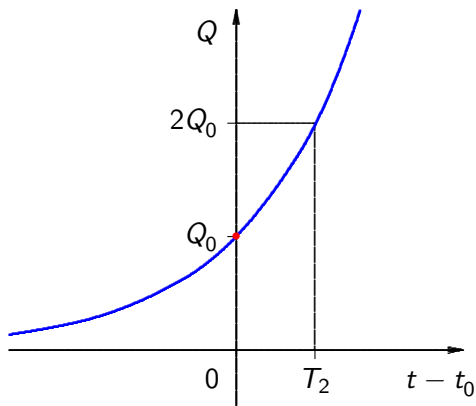
$$\ln \left(\frac{Q(t)}{Q_0} \right) = k(t - t_0)$$

$k > 0$: exponential growth, doubling time $T_2 = \ln(2)/k$ (time interval for increase from Q_0 to $2Q_0$; it took infinitely long to reach Q_0 at time t_0 ; “shortening of the future”)

$k < 0$: exponential decay, “half life” $T_{1/2} = \ln(1/2)/k = -\ln(2)/k$ (time interval for decrease from Q_0 to $Q_0/2$; it takes infinitely long for Q_0 to vanish)

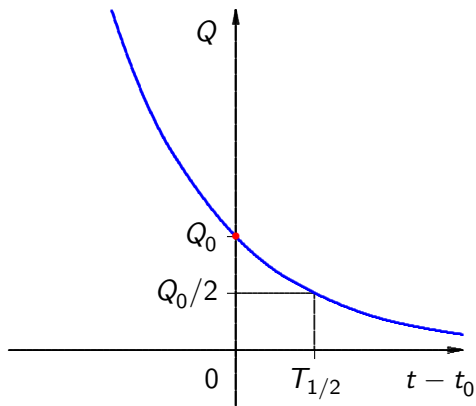
Some simple (and naïve) growth laws (contd)

Exponential growth ($k > 0$)



doubling time $T_2 = \ln(2)/k$
(took infinitely long to reach Q_0 at time t_0)

Exponential decay ($k < 0$)



"half life" $T_{1/2} = \ln(1/2)/k = -\ln(2)/k$
(takes infinitely long for Q_0 to vanish completely)

No finite real system can actually follow such behaviour over an arbitrarily long period of time!

Some simple (and naïve) growth laws (contd)

- ▶ **Limited growth/decay** ($k > 0$ rate constant, SI unit $[k] = s^{-1}$, constant limiting size $S > 0$):
Differential equation:

$$\dot{Q} = k(S - Q)$$

$$\dot{Q} + kQ = kS$$

Integrated forms:

$$Q(t) = S - (S - Q_0) \exp[-k(t - t_0)] \quad (Q_0 = Q(t_0), S = \lim_{t \rightarrow \infty} Q(t))$$

– linearized:

$$\ln \left(\frac{Q(t) - S}{Q_0 - S} \right) = -k(t - t_0)$$

$Q < S \Leftrightarrow \dot{Q} > 0$: growth towards limiting size S (“saturation limit”, “system capacity”)

$Q > S \Leftrightarrow \dot{Q} < 0$: decay towards limiting size S (“saturation limit”, “system capacity”)

The deviation from $S = \lim_{t \rightarrow \infty} Q(t)$ vanishes exponentially

Important question: What is (the best/right/correct value for) S ?

Note also: $Q(t)$ diverges, either to $+\infty$ or to $-\infty$, as we look into the past, i. e. when $t \rightarrow -\infty$!

Chemical kinetics (some instructive examples)

A, B, \dots

n different types of stuff ... countable (e.g. individuals) or measurable (mass, amount of substance), alternatively: densities of that stuff (number/amount per area/volume, assuming area/volume to be constant, i.e. time-independent) — assuming differentiability (even in case of countable stuff)

$k > 0, k_i > 0$

rate constants, elements of a singular non-symmetric $n \times n$ rate constant matrix $\underline{\underline{K}}$ (has no inverse $\underline{\underline{K}}^{-1}$)

Coupled set of first-order ODEs with initial conditions (conditions at time $t = t_0$):

$$\frac{d}{dt} \begin{pmatrix} A \\ B \\ \vdots \end{pmatrix} = \underline{\underline{K}} \begin{pmatrix} A \\ B \\ \vdots \end{pmatrix} \quad \text{with} \quad \begin{pmatrix} A \\ B \\ \vdots \end{pmatrix} \Big|_{t_0=0} = \begin{pmatrix} A_0 \\ B_0 \\ \vdots \end{pmatrix} \quad (1)$$

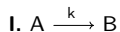
This has solutions of form $\underline{x} e^{\lambda t}$ with (λ, \underline{x}) obtained from the – possibly generalized ($p \geq 2$, see below) – eigenvalue problem of $\underline{\underline{K}}$: Denote $\underline{\underline{X}} = (\underline{x}_1, \dots, \underline{x}_n)$ and $\underline{\underline{\Lambda}} = \text{diag}(\lambda_1, \dots, \lambda_n)$, then

$$(\underline{\underline{K}} - \lambda_i \underline{\underline{E}})^p \underline{x}_i = \underline{0} \quad \Rightarrow \quad \text{if } p = 1: \underline{\underline{K}} \underline{\underline{X}} = \underline{\underline{X}} \underline{\underline{\Lambda}} \Leftrightarrow \underline{\underline{X}}^{-1} \underline{\underline{K}} \underline{\underline{X}} = \underline{\underline{\Lambda}}$$

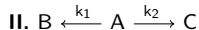
If $\lambda_i \neq \lambda_j$ for all $i \neq j$, the complete solution of eq. (1) is:

$$\begin{pmatrix} A \\ B \\ \vdots \end{pmatrix} = \sum_i c_i \underline{x}_i e^{\lambda_i t}; \quad \text{initial condition} \quad \begin{pmatrix} A_0 \\ B_0 \\ \vdots \end{pmatrix} = \sum_i c_i \underline{x}_i = \underline{\underline{X}} \begin{pmatrix} c_1 \\ \vdots \\ c_n \end{pmatrix} \quad \text{gives} \quad \begin{pmatrix} c_1 \\ \vdots \\ c_n \end{pmatrix} = \underline{\underline{X}}^{-1} \begin{pmatrix} A_0 \\ B_0 \\ \vdots \end{pmatrix}$$

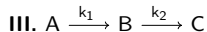
Chemical kinetics (some instructive examples, contd.)



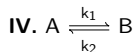
two compounds, a single reaction (only forward)



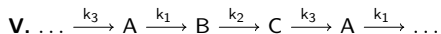
three compounds, two parallel reactions (both only forward)



three compounds (or resource/product/waste), two consecutive reactions (both only forward)



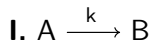
two compounds, two reactions (forward and reverse) – or a 2-loop



three compounds (or resource/product/waste), three consecutive reactions (all only forward), cyclic – or a 3-loop

All good things come in threes. (A, B, C)

Chemical kinetics (some instructive examples, contd.)



$$\left. \begin{array}{l} \dot{A} = -kA \\ \dot{B} = kA \end{array} \right\} \equiv \left\{ \frac{d}{dt} \begin{pmatrix} A \\ B \end{pmatrix} = \underline{\underline{K}} \begin{pmatrix} A \\ B \end{pmatrix}, \quad \underline{\underline{K}} = \begin{pmatrix} -k & 0 \\ k & 0 \end{pmatrix} \right.$$

Solving the eigenvalue problem of $\underline{\underline{K}}$:

$$\underline{\underline{X}}^{-1} \underline{\underline{K}} \underline{\underline{X}} = \underline{\underline{X}}^{-1} \underline{\underline{K}} (\underline{x}_1, \underline{x}_2) = \begin{pmatrix} 1 & 0 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} -k & 0 \\ k & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ -1 & 1 \end{pmatrix} = \begin{pmatrix} -k & 0 \\ 0 & 0 \end{pmatrix} = \text{diag}(-k, 0) = \text{diag}(\lambda_1, \lambda_2) = \underline{\underline{\Lambda}}$$

Solving the chemical kinetics problem:

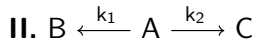
$$\begin{pmatrix} A \\ B \end{pmatrix} = A_0 \begin{pmatrix} 1 \\ -1 \end{pmatrix} e^{-kt} + (A_0 + B_0) \begin{pmatrix} 0 \\ 1 \end{pmatrix} \xrightarrow{t \rightarrow \infty} \lim_{t \rightarrow \infty} \begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} 0 \\ A_0 + B_0 \end{pmatrix}$$

or component-wise:

$$A(t) = A_0 e^{-kt}; \quad B(t) = A_0 (1 - e^{-kt}) + B_0$$

At the end (of time), compound A has completely vanished and only compound B is present, in total amount $A_0 + B_0$.

Chemical kinetics (some instructive examples, contd.)



$$\left. \begin{aligned} \dot{A} &= -k_1 A - k_2 A = -(k_1 + k_2)A \\ \dot{B} &= k_1 A \\ \dot{C} &= k_2 A \end{aligned} \right\} \equiv \left\{ \frac{d}{dt} \begin{pmatrix} A \\ B \\ C \end{pmatrix} = \underline{\underline{K}} \begin{pmatrix} A \\ B \\ C \end{pmatrix}, \quad \underline{\underline{K}} = \begin{pmatrix} -(k_1 + k_2) & 0 & 0 \\ k_1 & 0 & 0 \\ k_2 & 0 & 0 \end{pmatrix} \right.$$

Solving the eigenvalue problem of $\underline{\underline{K}}$:

$$\underline{\underline{X}}^{-1} \underline{\underline{K}} \underline{\underline{X}} = \begin{pmatrix} 1 & 0 & 0 \\ k_1/(k_1 + k_2) & 1 & 0 \\ k_2/(k_1 + k_2) & 0 & 1 \end{pmatrix} \begin{pmatrix} -(k_1 + k_2) & 0 & 0 \\ k_1 & 0 & 0 \\ k_2 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ -k_1/(k_1 + k_2) & 1 & 0 \\ -k_2/(k_1 + k_2) & 0 & 1 \end{pmatrix} = \begin{pmatrix} -(k_1 + k_2) & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \underline{\underline{\Lambda}}$$

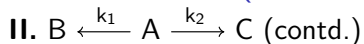
Solving the chemical kinetics problem:

$$\begin{pmatrix} A \\ B \\ C \end{pmatrix} = \frac{A_0}{k_1 + k_2} \begin{pmatrix} k_1 + k_2 \\ -k_1 \\ -k_2 \end{pmatrix} e^{-(k_1 + k_2)t} + \left(A_0 \frac{k_1}{k_1 + k_2} + B_0 \right) \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} + \left(A_0 \frac{k_2}{k_1 + k_2} + C_0 \right) \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

or component-wise:

$$A(t) = A_0 e^{-(k_1 + k_2)t}; \quad B(t) = A_0 \frac{k_1}{k_1 + k_2} \left(1 - e^{-(k_1 + k_2)t} \right) + B_0; \quad C(t) = A_0 \frac{k_2}{k_1 + k_2} \left(1 - e^{-(k_1 + k_2)t} \right) + C_0$$

Chemical kinetics (some instructive examples, contd.)



At every moment in time, the ratio of amounts of compounds B and C generated by the two reactions is constant:

$$\frac{B(t) - B_0}{C(t) - C_0} = \frac{k_1}{k_2} = \lim_{t \rightarrow \infty} \frac{B(t) - B_0}{C(t) - C_0}$$

At the end (of time), compound A has completely vanished and only the compounds B and C are present:

$$\lim_{t \rightarrow \infty} \begin{pmatrix} A \\ B \\ C \end{pmatrix} = \left(0, A_0 \frac{k_1}{k_1 + k_2} + B_0, A_0 \frac{k_2}{k_1 + k_2} + C_0 \right)^T$$

Chemical kinetics (some instructive examples, contd.)

III. $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ ("resource \rightarrow product \rightarrow waste")

$$\left. \begin{aligned} \dot{A} &= -k_1 A \\ \dot{B} &= k_1 A - k_2 B \\ \dot{C} &= k_2 B \end{aligned} \right\} \equiv \left\{ \frac{d}{dt} \begin{pmatrix} A \\ B \\ C \end{pmatrix} = \underline{\underline{K}} \begin{pmatrix} A \\ B \\ C \end{pmatrix}, \quad \underline{\underline{K}} = \begin{pmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{pmatrix} \right.$$

III.a $k_1 \neq k_2$:

Solving the eigenvalue problem of $\underline{\underline{K}}$:

$$\underline{\underline{X}}^{-1} \underline{\underline{K}} \underline{\underline{X}} = \begin{pmatrix} 1 & 0 & 0 \\ k_1/(k_1 - k_2) & 1 & 0 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ -k_1/(k_1 - k_2) & 1 & 0 \\ k_2/(k_1 - k_2) & -1 & 1 \end{pmatrix} = \begin{pmatrix} -k_1 & 0 & 0 \\ 0 & -k_2 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \underline{\underline{\Lambda}}$$

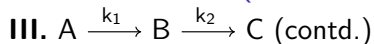
Solving the chemical kinetics problem:

$$\begin{pmatrix} A \\ B \\ C \end{pmatrix} = \frac{A_0}{k_1 - k_2} \begin{pmatrix} k_1 - k_2 \\ -k_1 \\ k_2 \end{pmatrix} e^{-k_1 t} + \left(A_0 \frac{k_1}{k_1 - k_2} + B_0 \right) \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix} e^{-k_2 t} + (A_0 + B_0 + C_0) \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

or component-wise: $A(t) = A_0 e^{-k_1 t}$;

$$B(t) = A_0 \frac{k_1}{k_1 - k_2} \left(e^{-k_2 t} - e^{-k_1 t} \right) + B_0 e^{-k_2 t}; \quad C(t) = A_0 \left(1 + \frac{k_2}{k_1 - k_2} e^{-k_1 t} - \frac{k_1}{k_1 - k_2} e^{-k_2 t} \right) + B_0 \left(1 - e^{-k_2 t} \right) + C_0$$

Chemical kinetics (some instructive examples, contd.)



Assuming $B_0 = 0$, the stationarity condition for B ($\dot{B} = 0$) leads to $B = \frac{k_1}{k_2}A$. This is fulfilled at time

$$t_{\hat{B}} = \frac{1}{k_2 - k_1} \ln \left(\frac{k_2}{k_1} \right) \quad (\text{the maximum amount of compound B is available at just this time}).$$

III.b $k_1 = k_2 = k$ (set $k_2 - k_1 = \varepsilon$, then take limits for $\varepsilon \rightarrow 0$):

Solutions for the chemical kinetics problem:

$$A(t) = A_0 e^{-kt}; \quad B(t) = (A_0 kt + B_0) e^{-kt}; \quad C(t) = A_0 (1 - (1 + kt) e^{-kt}) + B_0 (1 - e^{-kt}) + C_0$$

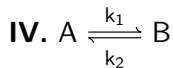
Assuming again $B_0 = 0$, the stationarity condition for B (see above) now requires that $B = A$. This is fulfilled at time $t_{\hat{B}} = \frac{1}{k}$ (at just this time the maximum amount of compound B is available).

Remark: The case $k_1 = k_2$ requires consideration of a generalized eigenvalue problem for \underline{K} . This leads to a matrix in Jordan normal form (instead of a diagonal matrix):

$$\underline{X}^{-1} \underline{K} \underline{X} = \begin{pmatrix} k & 0 & 0 \\ 0 & 1 & 0 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} -k & 0 & 0 \\ k & -k & 0 \\ 0 & k & 0 \end{pmatrix} \begin{pmatrix} 1/k & 0 & 0 \\ 0 & 1 & 0 \\ -1/k & -1 & 1 \end{pmatrix} = \begin{pmatrix} -k & 0 & 0 \\ \mathbf{1} & -k & 0 \\ 0 & 0 & 0 \end{pmatrix} = \underline{J}$$

In all cases, the compounds A and B have completely vanished at the end (of time) and only compound C is present, in total amount $A_0 + B_0 + C_0$.

Chemical kinetics (some instructive examples, contd.)



$$\left. \begin{aligned} \dot{A} &= -k_1 A + k_2 B \\ \dot{B} &= k_1 A - k_2 B \end{aligned} \right\} \equiv \left\{ \frac{d}{dt} \begin{pmatrix} A \\ B \end{pmatrix} = \underline{K} \begin{pmatrix} A \\ B \end{pmatrix}, \quad \underline{K} = \begin{pmatrix} -k_1 & k_2 \\ k_1 & -k_2 \end{pmatrix} \right.$$

Solving the eigenvalue problem of \underline{K} :

$$\underline{X}^{-1} \underline{K} \underline{X} = \frac{k_1}{k_1 + k_2} \begin{pmatrix} 1 & -k_2/k_1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} -k_1 & k_2 \\ k_1 & -k_2 \end{pmatrix} \begin{pmatrix} 1 & k_2/k_1 \\ -1 & 1 \end{pmatrix} = \begin{pmatrix} -(k_1 + k_2) & 0 \\ 0 & 0 \end{pmatrix} = \underline{\Lambda}$$

Solving the chemical kinetics problem:

$$\begin{pmatrix} A \\ B \end{pmatrix} = \frac{1}{k_1 + k_2} (A_0 k_1 - B_0 k_2) \begin{pmatrix} 1 \\ -1 \end{pmatrix} e^{-(k_1 + k_2)t} + \frac{k_1}{k_1 + k_2} (A_0 + B_0) \begin{pmatrix} k_2/k_1 \\ 1 \end{pmatrix} \xrightarrow{t \rightarrow \infty} \lim_{t \rightarrow \infty} \begin{pmatrix} A \\ B \end{pmatrix} = \frac{A_0 + B_0}{k_1 + k_2} \begin{pmatrix} k_2 \\ k_1 \end{pmatrix}$$

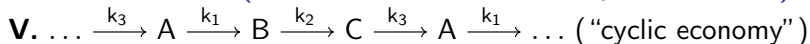
$$A(t) = \frac{A_0 k_2}{k_1 + k_2} \left(1 + \frac{k_1}{k_2} e^{-(k_1 + k_2)t} \right) + \frac{B_0 k_2}{k_1 + k_2} \left(1 - e^{-(k_1 + k_2)t} \right)$$

$$B(t) = \frac{A_0 k_1}{k_1 + k_2} \left(1 - e^{-(k_1 + k_2)t} \right) + \frac{B_0 k_1}{k_1 + k_2} \left(1 + \frac{k_2}{k_1} e^{-(k_1 + k_2)t} \right)$$

At the end (of time), compounds A and B are both present, not in equal amounts (amount ratio $A/B = 1$) but in amount ratio

$$\lim_{t \rightarrow \infty} \frac{A(t)}{B(t)} = \frac{k_2}{k_1}$$

Chemical kinetics (some instructive examples, contd.)



$$\left. \begin{aligned} \dot{A} &= -k_1 A + k_3 C \\ \dot{B} &= k_1 A - k_2 B \\ \dot{C} &= k_2 B - k_3 C \end{aligned} \right\} \equiv \left\{ \frac{d}{dt} \begin{pmatrix} A \\ B \\ C \end{pmatrix} = \underline{\underline{K}} \begin{pmatrix} A \\ B \\ C \end{pmatrix}, \quad \underline{\underline{K}} = \begin{pmatrix} -k_1 & 0 & k_3 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & -k_3 \end{pmatrix} \right.$$

Solving the eigenvalue problem of $\underline{\underline{K}}$:

$$0 = \det(\underline{\underline{K}} - \lambda \underline{\underline{E}}) = -\lambda (\lambda^2 + (k_1 + k_2 + k_3)\lambda + (k_1 k_2 + k_2 k_3 + k_3 k_1))$$

$$\lambda_{1,2} = -\frac{1}{2}(k_1 + k_2 + k_3) \pm \frac{1}{2}\sqrt{D}; \quad \lambda_3 = 0$$

with discriminant $D = k_1^2 + k_2^2 + k_3^2 - 2(k_1 k_2 + k_2 k_3 + k_3 k_1)$.

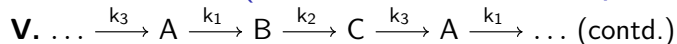
- (i) $D = 0$ ($\lambda_1 = \lambda_2 \in \mathbb{R}$) describes a cone in the 1st octant ($k_1 > 0, k_2 > 0, k_3 > 0$) with apex at the origin and rotation axis along the space diagonal $(k_1, k_2, k_3)^T = \alpha(1, 1, 1)^T$, which touches the coordinate system planes ($k_j = 0$) along their angle-bisecting diagonal lines ($k_j = k_l, j \neq i \neq l$).
- (ii) $D < 0$ ($\lambda_1 = \lambda_2^* \in \mathbb{C}$) inside that cone.
- (iii) $D > 0$ ($\lambda_1 \neq \lambda_2 \in \mathbb{R}$) in the remaining parts of the 1st octant outside the cone.

If $\lambda_1 \neq \lambda_2$:

$$\underline{\underline{X}} = (\underline{x}_1, \underline{x}_2, \underline{x}_3) = \begin{pmatrix} (\lambda_2 + k_1)/k_2 & (\lambda_1 + k_1)/k_2 & k_3/k_1 \\ (\lambda_2 + k_3)/k_2 & (\lambda_2 + k_3)/k_2 & k_3/k_2 \\ 1 & 1 & 1 \end{pmatrix}, \quad \underline{\underline{\Lambda}} = \text{diag}(\lambda_1, \lambda_2, 0)$$

$$\det(\underline{\underline{X}}) = \frac{\lambda_2 - \lambda_1}{k_1 k_2^2} (k_1^2 + (\lambda_1 + \lambda_2)k_1 - k_2 k_3) = \frac{\sqrt{D}}{k_2} \left(\frac{k_3}{k_1} + \frac{k_3}{k_2} + 1 \right)$$

Chemical kinetics (some instructive examples, contd.)



Form of solutions for the chemical kinetics problem ($\lambda_1 \neq \lambda_2$, assuming $\operatorname{Re}(\lambda_i) < 0$):

$$\begin{pmatrix} A \\ B \\ C \end{pmatrix} = c_1 \underline{x}_1 e^{\lambda_1 t} + c_2 \underline{x}_2 e^{\lambda_2 t} + c_3 \begin{pmatrix} k_3/k_1 \\ k_3/k_2 \\ 1 \end{pmatrix} \in \mathbb{R}^3$$

This contains exponentially decaying parts for $D \geq 0$ (λ_1, λ_2 both real) and exponentially damped oscillating parts for $D < 0$ ($\lambda_1 = \lambda_2^* \in \mathbb{C}$).

At the end (of time), the amounts of compounds A, B and C are

$$\lim_{t \rightarrow \infty} \begin{pmatrix} A \\ B \\ C \end{pmatrix} = c_3 \begin{pmatrix} k_3/k_1 \\ k_3/k_2 \\ 1 \end{pmatrix} = \frac{c_3}{k_1 k_2} \begin{pmatrix} k_2 k_3 \\ k_3 k_1 \\ k_1 k_2 \end{pmatrix}$$

Equal amounts of compounds A, B and C are expected (or, more important perhaps, cannot be avoided) iff (if and only if) all rate constants k_i are equal:

$$\lim_{t \rightarrow \infty} \begin{pmatrix} A \\ B \\ C \end{pmatrix} = c_3 \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \quad (k_1 = k_2 = k_3)$$

To be included in the next edition:

▶ non-linear ODEs:

- hyperbolic growth $\dot{Q} = \alpha Q^2$

(growth exceeding any limit [or explosion] in *finite* time, in contrast to exponential growth, which does the same, but requires infinite time)

- logistic growth (P Verhulst, 19th century) $\dot{Q} = r Q - s Q^2$

(a description of “natural growth” valid for all times t , i.e. $-\infty < t < +\infty$)

- predator-prey models (Lotka & Volterra, 1920s/1930s)

- Daisyworld model (Watson & Lovelock, 1980s)

▶ PDEs:

- diffusion models (point source, etc.) *

- ...

* G Vogl: Wandern ohne Ziel — Von der Atomdiffusion zur Ausbreitung von Lebewesen und Ideen, Springer, 2007, <https://doi.org/10.1007/978-3-540-71064-6> (only in German)

Finale

Two quotes from Einstein (1930/1936)

From the opening address for the 7th German Radio Broadcasting Exhibition, 22 Aug 1930, Berlin

Sollen sich auch alle schämen, die gedankenlos sich der Wunder der Wissenschaft und Technik bedienen und nicht mehr davon geistig erfasst haben als die Kuh von der Botanik der Pflanzen, die sie mit Wohlbehagen frisst.

English translation:

Shall all be ashamed who thoughtlessly make use of the wonders of science and technology and have not intellectually grasped more of it than has the cow of the botany of plants, which it eats with pleasure.

Full text:

F. Herneck, *Naturwissenschaften* 48 (1961) 33
HJ Küpper, <https://einstein-website.de/tondokument/> or <https://einstein-website.de/en/sound-document/> (short audio file included, accessed 14 May 2024)

and will endure as long as there exists a civilized community on this earth."

On 1 May 1936 a prominent American publisher wrote to ask Einstein a favor. The publisher had just broken ground for a new library wing for his country home and wanted to place in the cornerstone an airtight metal box containing items that would be of archeological interest to posterity. There would be, for example, an issue of the *New York Times* specially printed on long-lasting rag paper. He asked Einstein to contribute a message and enclosed, for Einstein to write it on, a sheet of coupon bond paper made out of rag stock that, he assured Einstein, was expected to last a thousand years.

On 4 May 1936 Einstein sent the following message, presumably typed on the special, long-lasting paper:

Dear Posterity,

If you have not become more just, more peaceful, and generally more rational than we are (or were)—why then, the Devil take you.

Having, with all respect, given utterance to this pious wish,

I am (or was),

Your,

Albert Einstein

A correspondent asked Einstein two questions. The first was whether he owed anything to so-called specu-

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Quick demonstration(s) with objects from everyday life (if time permits)

Take-home messages

- ▶ Only three types of thermodynamic systems exist (isolated, closed, open)
- ▶ Chemical potential μ and entropy S are the essential central thermodynamic quantities
- ▶ Flow of matter/energy is unavoidably linked to “losses” (entropy production).
- ▶ Systems close to equilibrium (linear regime) follow certain rules (\rightarrow Onsager reciprocal relations, \rightarrow Prigogine’s principle of minimal entropy production)
- ▶ Systems far away from equilibrium may generate “quite naturally” new structures (dissipative structures), e.g. Bénard convection, Belousov-Zhabotinsky reaction, living cells
- ▶ (Systems of coupled) differential equations allow us to describe (to model, to understand?) time evolution of real-world systems
- ▶ Take care for yourself — and for the planet, (try to) act responsibly, (try to) be a catalyst for change in a “good” direction*



Scene from WALL·E, Pixar & Disney, 2008

„Die mit Abstand größte Gefahr Künstlicher Intelligenz besteht darin, dass die Menschen zu früh zu dem Schluss kommen, dass sie sie verstehen.“

-ELIEZER YUDKOWSKY



Quote from E Yudkowsky, Founder of Friendly AI

* Who decides what is “good” and what is “bad”? (Relevance of [quality] level of education? Type of society? Type of political system? AI tasks?)