LECTURE 07

Modeling of Chemical Reactions

Department of Analytical, Colloidal Chemistry and Technology of Rare Elements

Modeling of chemico-technological processes | 6B07102 Chemical Engineering

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Purpose and expected learning outcomes

Purpose: turn a reaction scheme and kinetic data into a quantitative model that predicts concentration, yield and selectivity.

DISTINGUISH

Stoichiometry, rate law and equilibrium: three different pieces of information.

DETERMINE

Reaction orders and k from initial-rate and integral analysis of data.

CALCULATE

Activation energy, half-life, t_{90} and equilibrium conversion.

FORMULATE

Batch balances for single, consecutive, parallel and reversible reactions.

INTEGRATE

Kinetic ODEs numerically and recognise stiffness and instability.

OPTIMIZE

Temperature and pressure for yield, selectivity and rate (Haber–Bosch).

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From reaction scheme to process decision

01 Reaction scheme
Stoichiometry, network, species

02 Rate law
Orders and k from experiments

03 Temperature
Arrhenius parameters A, Ea

04 Balances
$dC/dt = \Sigma \nu_{ij} r_j$ for a batch reactor

05 Solve
Analytical or stiff ODE solver

06 Decide
T, P, time for yield and selectivity

Industrial relevance: ammonia synthesis • fine-chemical batch reactors • pharmaceuticals • polymerization • combustion

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Rate laws versus stoichiometry

Stoichiometric coefficients do not, in general, give the reaction orders.

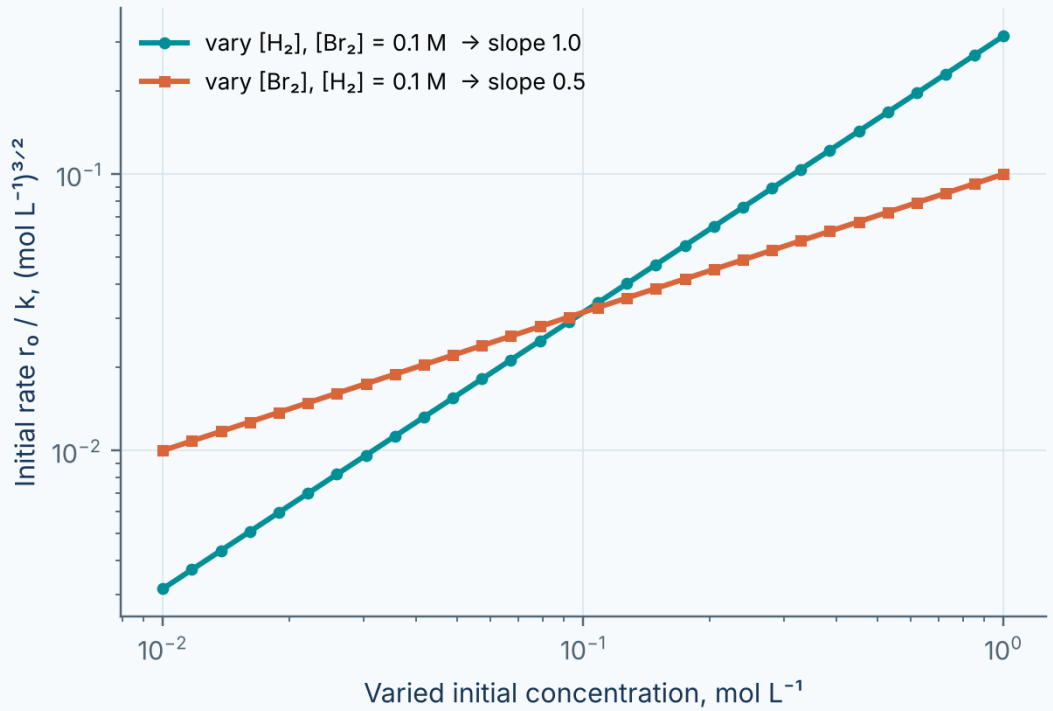
$$H_2 + Br_2 \rightarrow 2HBr$$

$$r = k[H_2][Br_2]^{1/2} / (1 + k'[HBr]/[Br_2])$$

MODEL CONDITIONS The rate law of this chain reaction follows from its radical mechanism (Br•, H•) and was confirmed by experiment; it is not elementary.

EXAMPLE Initial-rate method ([HBr] = 0): log r_0 vs log[H_2] has slope 1, log r_0 vs log[Br_2] has slope 0.5. A 2:1 stoichiometry predicts neither.

EXAMPLE · INITIAL-RATE METHOD, log–log PLOT



ENGINEERING INTERPRETATION Orders come from experiment or mechanism; HBr inhibition (k' term) matters only at higher conversion.

Further reading: Fogler, Elements of Chemical Reaction Engineering, 6th ed. (2020), ch. 3, 5–8; Levenspiel, Chemical Reaction Engineering, 3rd ed. (1999), ch. 2–3, 7–8.

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Integral method: testing a rate law

Integrated rate laws turn the right model into a straight line.

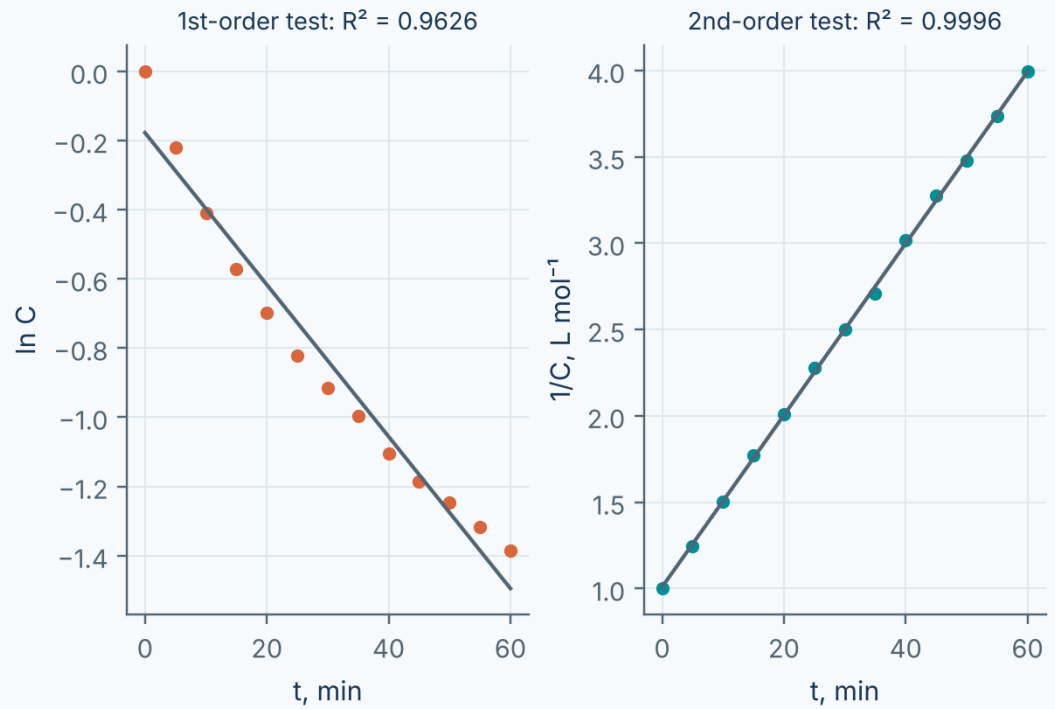
1st order: $\ln C = \ln C_0 - kt$

2nd order: $1/C = 1/C_0 + kt$

MODEL CONDITIONS Isothermal batch data, single reactant, C_0 = 1.0 mol L^{-1}, sampled every 5 min (synthetic data with 1.2 % noise).

EXAMPLE ln C vs t is curved (R^2 = 0.963); 1/C vs t is linear (R^2 = 0.9996) with slope k = 0.050 L mol^{-1} min^{-1}. The reaction is second order.

EXAMPLE · SAME DATA, TWO LINEARIZATIONS



ENGINEERING INTERPRETATION A high R^2 alone is weak evidence; inspect residuals and test over at least 2–3 half-lives.

Further reading: Fogler, Elements of Chemical Reaction Engineering, 6th ed. (2020), ch. 3, 5–8; Levenspiel, Chemical Reaction Engineering, 3rd ed. (1999), ch. 2–3, 7–8.

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Arrhenius temperature dependence

The activation energy sets how strongly k responds to temperature.

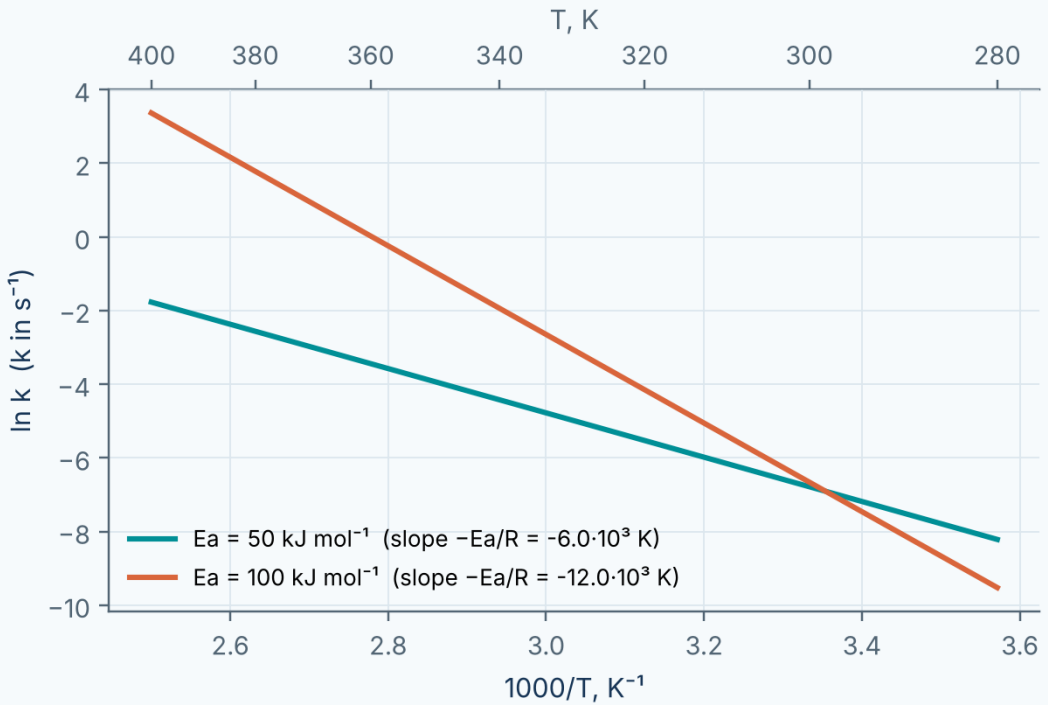
$$k = A \exp(-Ea/RT)$$

$$\ln(k_2/k_1) = (Ea/R)(1/T_1 - 1/T_2)$$

MODEL CONDITIONS Ea in J mol^{-1}, T in kelvin, Ea assumed constant over the fitted range.

EXAMPLE If k doubles between 25 and 35 °C, Ea = 52.9 kJ mol^{-1}. For Ea = 100 kJ mol^{-1} the same 10 K step multiplies k by 3.7.

EXAMPLE · ARRHENIUS PLOT, k(298 K) = 1·10^{-3} s^{-1}



ENGINEERING INTERPRETATION Fit ln k vs 1/T, not k vs T; a curved Arrhenius plot points to a change of mechanism or mass-transfer limitation.

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Batch reactor: the effect of reaction order

The species balance predicts the concentration history for a chosen rate law.

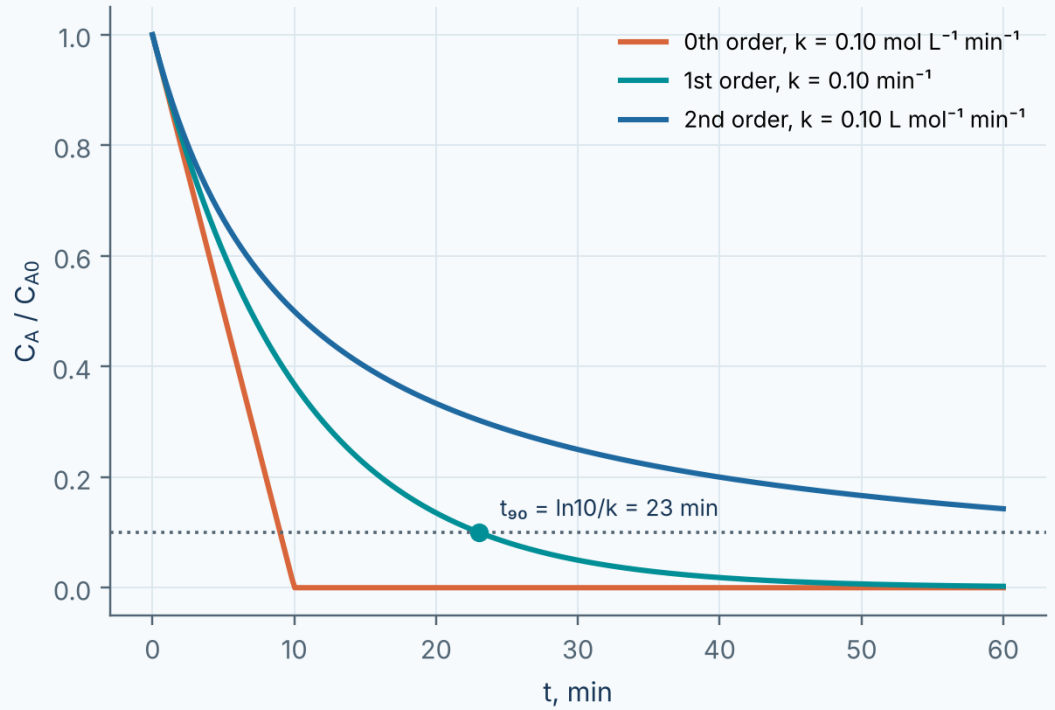
$$dC_A/dt = -k\,C_A^n$$

$$\text{1st order: } t_{90} = \ln 10 / k$$

MODEL CONDITIONS Closed, isothermal, well-mixed, constant volume. All three curves start at the same rate, 0.10 mol L^{-1} min^{-1}.

EXAMPLE First order, k = 0.10 min^{-1}: $t_{1/2}$ = 6.9 min, t_{90} = 23 min. Zero order reaches full conversion at 10 min; second order still has 14 % left at 60 min.

EXAMPLE · C_A/C_{A0} FOR n = 0, 1, 2



ENGINEERING INTERPRETATION Higher orders slow down strongly at high conversion, which dominates the batch time for the last few percent.

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Numerical integration of kinetic equations

Most networks have no analytical solution and are integrated step by step.

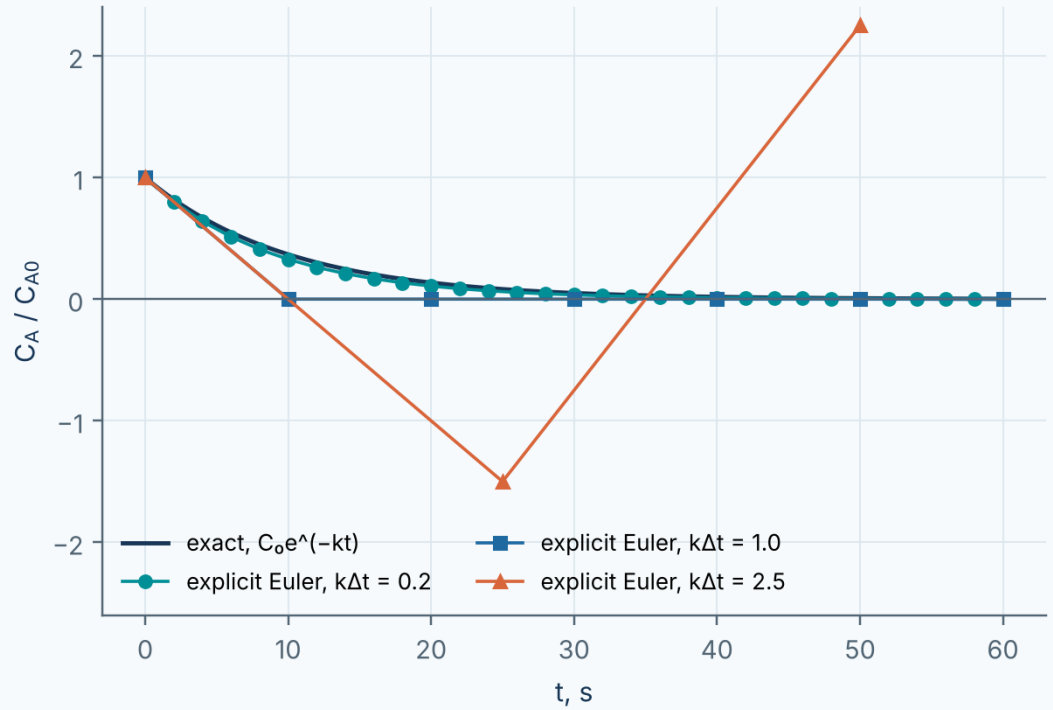
Euler: $C^{k+1} = C^k - k\Delta t \cdot C^k$

stable only if $k\Delta t < 2$

MODEL CONDITIONS A → B, $k = 0.1\ s^{-1}$, exact $C/C_0 = e^{-kt}$. The explicit Euler factor per step is $(1 - k\Delta t)$.

EXAMPLE $k\Delta t = 0.2$ follows the exact curve; $k\Delta t = 1.0$ gives $C = 0$ after one step; $k\Delta t = 2.5$ oscillates with growing amplitude and negative concentrations.

EXAMPLE · EXPLICIT EULER AT THREE TIME STEPS



ENGINEERING INTERPRETATION Same lesson as FTCS in Lecture 05: explicit schemes are conditionally stable; implicit ones are not limited.

Further reading: Hairer & Wanner, Solving Ordinary Differential Equations II: Stiff Problems (1996); Fogler (2020), ch. 8; COMSOL Chemical Reaction Engineering Module User's Guide.

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Consecutive reactions: maximizing an intermediate

When the product reacts further, there is an optimum reaction time.

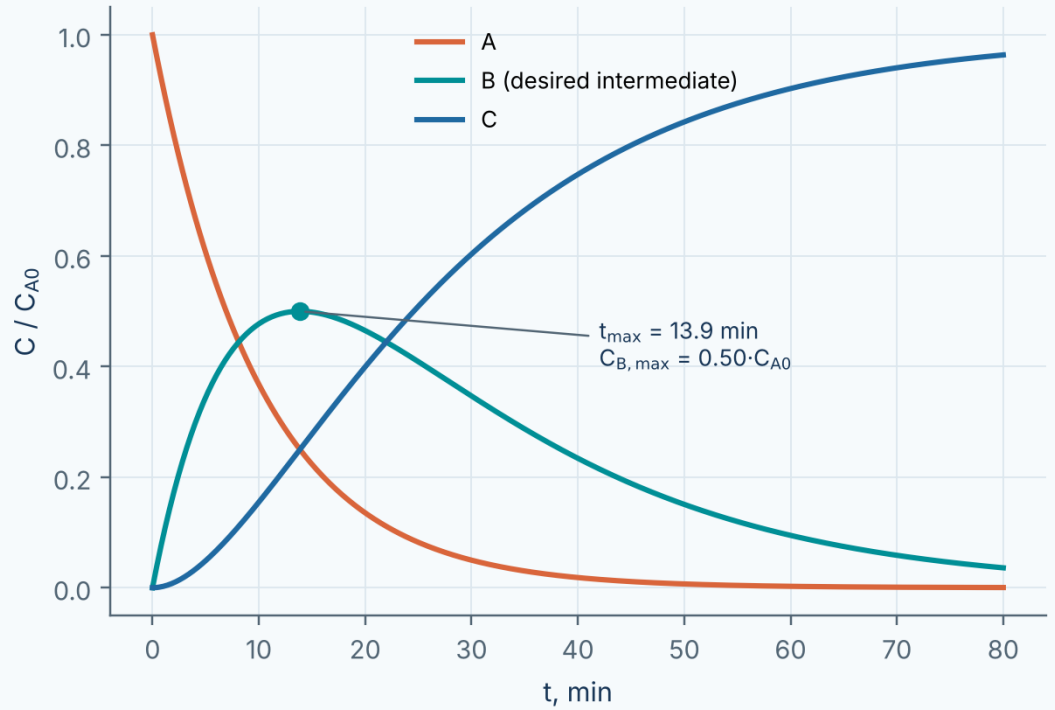
$$A \rightarrow B \rightarrow C \quad (k_1, k_2)$$

$$t_{max} = \ln(k_1/k_2) / (k_1 - k_2)$$

MODEL CONDITIONS First-order steps, batch, $C_{B0} = C_{C0} = 0$. $C_{B,max}/C_{A0} = (k_1/k_2)^{k_2/(k_2-k_1)}$.

EXAMPLE $k_1 = 0.10$ and $k_2 = 0.05\ min^{-1}$: B peaks at 13.9 min at $C_B = 0.50 \cdot C_{A0}$. After 60 min only 9 % B remains.

EXAMPLE · A → B → C, $k_1 = 2k_2$



ENGINEERING INTERPRETATION Stopping the batch (or sizing a PFR residence time) at t_{max} is the main design variable for intermediates.

Further reading: Fogler, Elements of Chemical Reaction Engineering, 6th ed. (2020), ch. 3, 5–8; Levenspiel, Chemical Reaction Engineering, 3rd ed. (1999), ch. 2–3, 7–8.

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Parallel reactions: temperature controls selectivity

Competing pathways share the reactant; their k values respond differently to T.

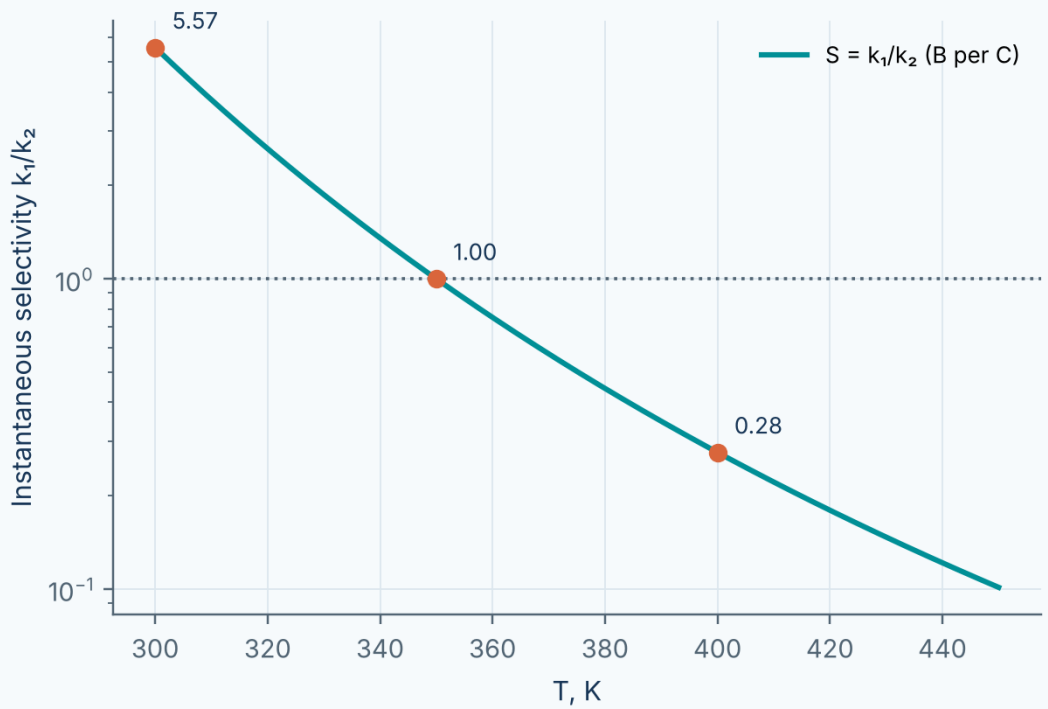
$$A \rightarrow B\ (k_1), \quad A \rightarrow C\ (k_2)$$

$$S = k_1/k_2 \propto \exp[-(Ea_1 - Ea_2)/RT]$$

MODEL CONDITIONS First-order steps, so the instantaneous selectivity is k_1/k_2 and does not depend on C_A.

EXAMPLE $Ea_1 = 60$, $Ea_2 = 90$ kJ mol^{-1}, equal rates at 350 K. S = 5.6 at 300 K but 0.28 at 400 K: heating favours the reaction with the higher Ea.

EXAMPLE · SELECTIVITY VS TEMPERATURE



ENGINEERING INTERPRETATION Low T gives selectivity but a slow rate; the optimum balances productivity against by-product removal cost.

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Equilibrium and Gibbs energy

Equilibrium limits conversion however fast the catalyst is.

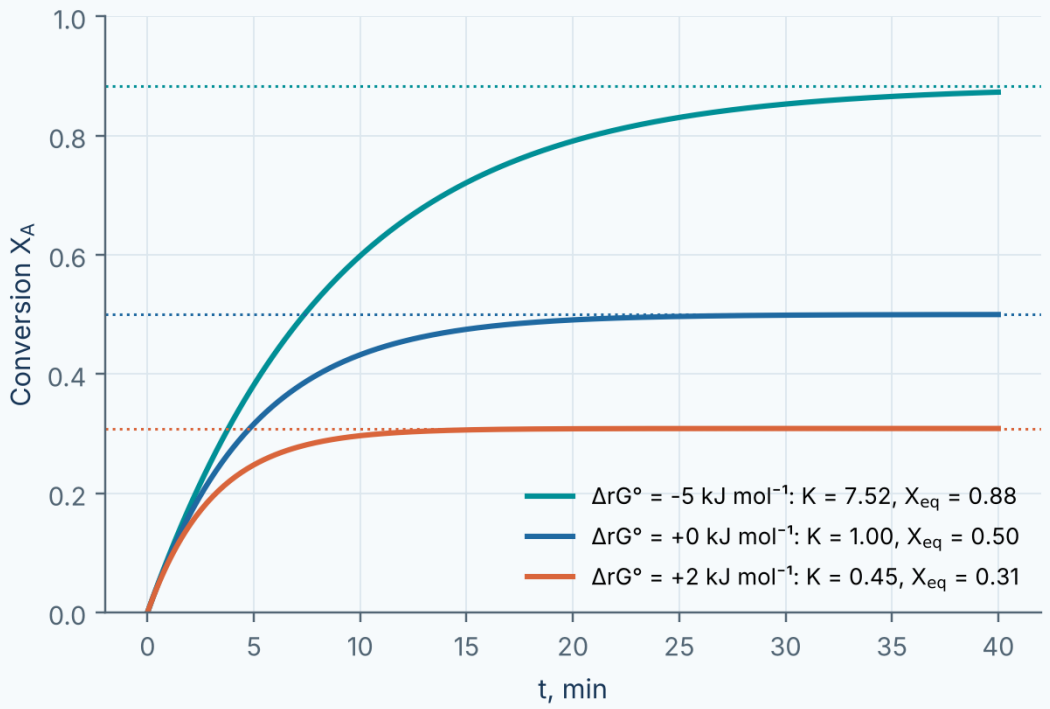
$$\Delta_r G^\circ = -RT \ln K$$

$$A \rightleftharpoons B: \; X_{eq} = K / (1 + K)$$

MODEL CONDITIONS K in terms of activities (dimensionless); first-order forward and reverse steps, $k_r = k_f/K$, $k_f = 0.1\ min^{-1}$, 298 K.

EXAMPLE $\Delta_r G^\circ = -5\ kJ\ mol^{-1}$ gives K = 7.5 and $X_{eq} = 0.88$; $\Delta_r G^\circ = +2\ kJ\ mol^{-1}$ still allows $X_{eq} = 0.31$. Approach rate is $k_f + k_r$.

EXAMPLE · APPROACH TO EQUILIBRIUM, A ⇌ B



ENGINEERING INTERPRETATION Kinetics decides how fast X approaches X_{eq}; thermodynamics decides where it stops.

Further reading: Atkins & de Paula, Physical Chemistry, ch. 6; Gillespie & Beattie, Phys. Rev. 36 (1930) 743; Appl, Ammonia, Ullmann's Encyclopedia of Industrial Chemistry.

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Haber–Bosch: the equilibrium trade-off

Ammonia synthesis is exothermic and reduces the number of gas moles.

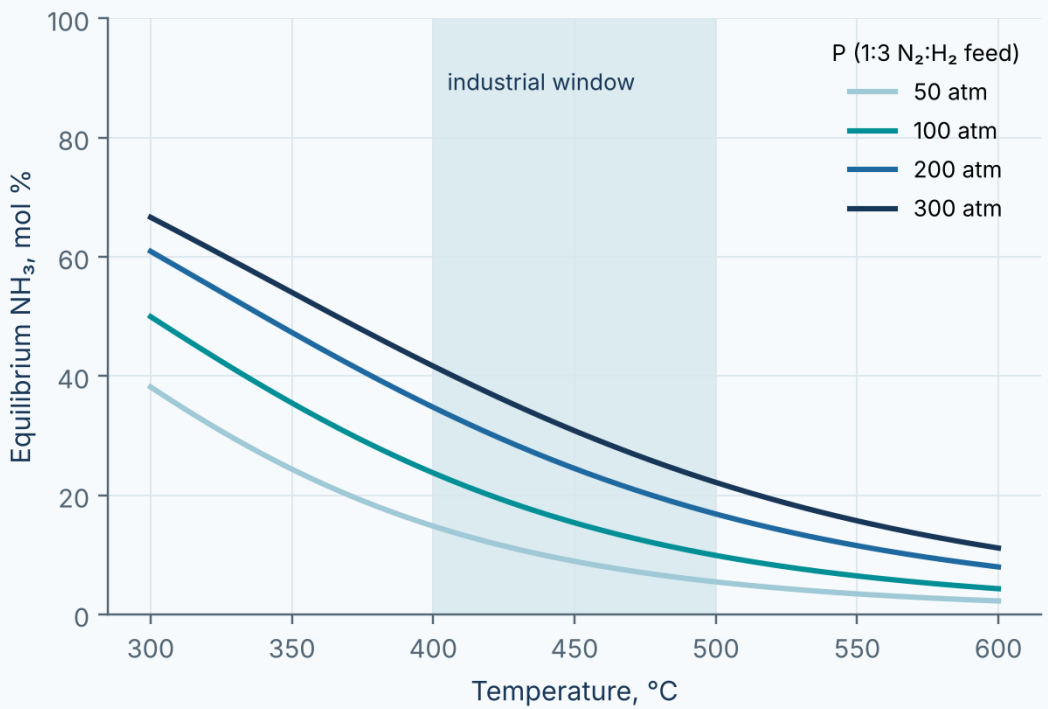
$$N_2 + 3H_2 \rightleftharpoons 2NH_3, \quad \Delta_r H^\circ \approx -92 \text{ kJ mol}^{-1}$$

$$y/(1-y)^2 = 0.325\, K_p P$$

MODEL CONDITIONS Ideal gas, N_2:H_2 = 1:3 feed, K_p for ½N_2 + 3/2H_2 ⇌ NH_3 from the Gillespie–Beattie correlation.

EXAMPLE At 200 atm: 34.8 % NH_3 at 400 °C, 24.5 % at 450 °C, 16.8 % at 500 °C (K_p(450 °C) = 6.6·10^{-3} atm^{-1}). Real-gas corrections raise these values slightly.

EXAMPLE · EQUILIBRIUM NH_3 VS T AND P



ENGINEERING INTERPRETATION Low T favours equilibrium but slows the Fe catalyst: plants run at 400–500 °C, 150–300 bar, with recycle.

Further reading: Atkins & de Paula, Physical Chemistry, ch. 6; Gillespie & Beattie, Phys. Rev. 36 (1930) 743; Appl, Ammonia, Ullmann's Encyclopedia of Industrial Chemistry.

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Reaction networks and stiffness

Networks are written in matrix form; widely different k values make them stiff.

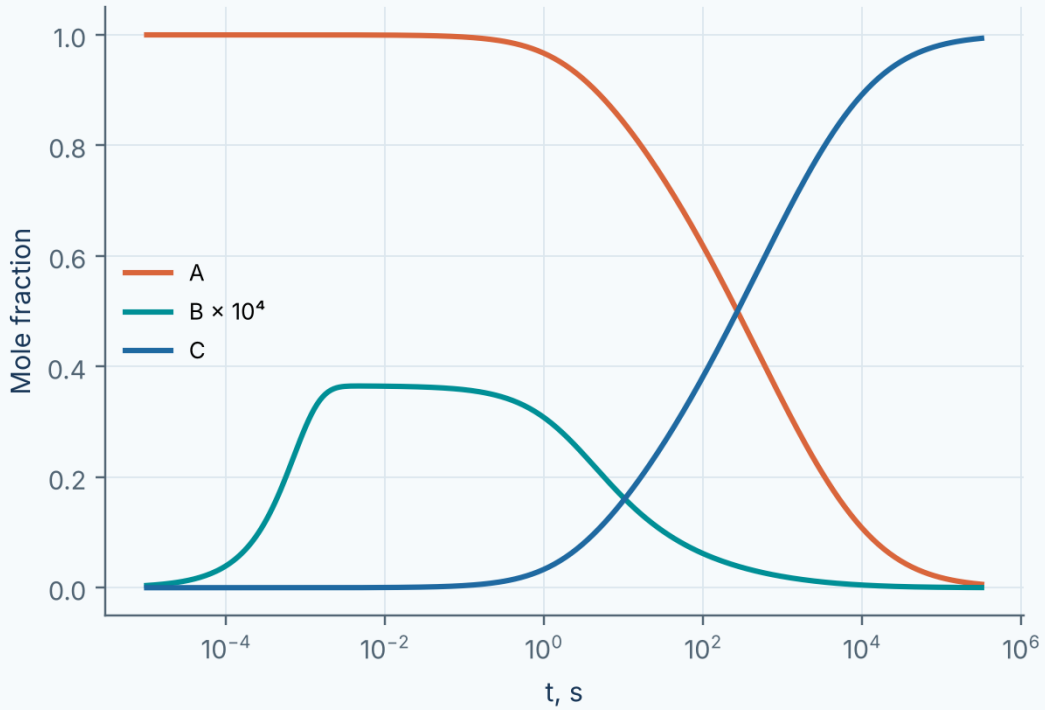
$$\frac{dC}{dt} = \nu^{T} r(C, T)$$

$$k = 0.04,\ 3\cdot10^{7},\ 10^{4}\ \text{(Robertson)}$$

MODEL CONDITIONS Robertson benchmark: A→B, 2B→B+C, B+C→A+C; k spans nine orders of magnitude; B stays below $4\cdot10^{-5}$ while A and C change over 10^{5} s.

EXAMPLE Explicit RK45 needs 34 543 steps just to reach t = 40 s; the implicit BDF solver needs 171 steps to 40 s and 425 to $4\cdot10^{5}$ s.

EXAMPLE · ROBERTSON PROBLEM, BDF SOLUTION



ENGINEERING INTERPRETATION Use implicit (BDF) solvers for kinetics, as COMSOL does by default; check for negative concentrations.

Further reading: Hairer & Wanner, Solving Ordinary Differential Equations II: Stiff Problems (1996); Fogler (2020), ch. 8; COMSOL Chemical Reaction Engineering Module User's Guide.

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Conclusions: a verified model is a useful model

PHYSICS

Stoichiometry fixes mass balance; the rate law and equilibrium must be measured or derived.

EQUATIONS

Batch balances $dC/dt = v^{T}r$; integrated forms test orders on data.

PARAMETERS

k, n, Ea and K carry uncertainty; fit them over the range of use.

NUMERICS

Explicit methods are conditionally stable; stiff networks need BDF.

SELECTIVITY

Reaction time and temperature control yield of intermediates and side products.

APPLICATION

Haber–Bosch shows the compromise between equilibrium and rate.

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Homework: calculations, interpretation and research

1. THEORY Explain why the $H_2 + Br_2$ rate law contains $[Br_2]^{1/2}$. Which elementary steps of the radical mechanism produce this order?

2. CALCULATION $k = 2.0 \cdot 10^{-3}$ s^{-1} at 300 K and $8.5 \cdot 10^{-3}$ s^{-1} at 320 K. Find Ea and A, then t_{90} at 310 K for a first-order reaction.

3. DATA Use the dataset L07_dataset.csv (t, C). Test zero, first and second order by the integral method and report k with its 95 % confidence interval.

4. CODE Integrate A → B → C ($k_1 = 0.2$, $k_2 = 0.05$ min^{-1}) with explicit Euler and with an implicit solver. Compare t_{max} and $C_{B,max}$ with the analytical values.

5. RESEARCH Recalculate the equilibrium NH_3 fraction at 450 °C and 100, 200 and 300 atm. Discuss why industrial converters stay far below equilibrium at the outlet.

Constants: R = 8.314 J mol^{-1} K^{-1}; T(25 °C) = 298.15 K; 1 atm = 101 325 Pa.

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Recommended Literature

1. Fogler, H. S. *Elements of Chemical Reaction Engineering*. 5th ed., Pearson, 2016.
2. Himmelblau, D. M., Riggs, J. B. *Basic Principles and Calculations in Chemical Engineering*. 8th ed., Pearson, 2012.
3. Bird, R. B., Stewart, W. E., Lightfoot, E. N. *Transport Phenomena*. 2nd ed., John Wiley & Sons, 2002.
4. Levenspiel, O. *Chemical Reaction Engineering*. 3rd ed., John Wiley & Sons, 1999.
5. Bequette, B. W. *Process Control: Modeling, Design, and Simulation*. Prentice Hall, 2003.