

BAE 820 Physical Principles of Environmental Systems

Acquisition of reaction rate data

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Uncertainties in real world reaction rate data

- Most interesting reaction systems involves multiple reactions, thus a lot of data are needed to cover a process.
- Many interesting reactions are catalytic, and different catalyst systems behave quite differently with different catalyst formations.
 - Sensitive to impurities, deactivation
 - Orders and activation energies vary with conditions
- High uncertainties
 - In most cases, reaction rate data can not be found in handbooks.
 - We have to reexamine every new reaction system from first principles.
 - We should be suspicious on any general correlation of reaction rates.
 - We often need to make estimates with several approximations.
 - The third decimal is almost always meaningless in reactor engineering.

Acquisition of reaction rate data

- For simple and well know process, there may be rate expressions in the literature that can be used.
- Sometimes rates or a reasonable rate expression can be estimated from a process similar to the one of interest.
- In rare cases, theoretical rate can be calculated based on statistics mechanics or quantum mechanics.
- In many cases, reaction rate data is obtained from experiments.

Thermodynamics and reactors

- One must know enough chemistry to decide what reactions should be expected with given reactants and conditions.
- Once one has formulated a list of possible reactions, one should look up the relevant free energy changes ΔG_R^0 in order to calculate equilibrium composition for the given feed and temperature. A chemical reaction cannot be made to produce a conversion beyond that of chemical equilibrium, $\Delta G=0$.

$$K_{\text{eq}} = \prod_{j=1}^S C_j^{\nu_j} = \frac{k_f}{k_b} = \exp(-\Delta G_R^0 / RT)$$

Where ΔG_R^0 is the Gibbs free energy change of the reaction in the standard state.

When $\Delta G_R^0 \ll 0$, the reaction should be expected to be irreversible.

Standard state enthalpy and free energy changes for some important reactions

| Reaction | $\Delta H_R^0, 298\text{K}$ kJ/mole | $\Delta G_R^0, 298\text{K}$ kJ/mole |
|--|--|--|
| $\text{N}_2 + \text{O}_2 \longrightarrow 2\text{NO}$ | +180.75 | +173.4 |
| $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$ | -114.14 | -70.785 |
| $2\text{NO} \longrightarrow \text{N}_2 + \text{O}_2$ | -180.75 | -173.4 |
| $\text{CH}_4 + 2\text{O}_2 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ | -802.32 | -800.78 |
| $\text{CO} + 1/2\text{O}_2 \longrightarrow \text{CO}_2$ | -282.99 | -257.12 |
| $\text{NH}_3 + 5/4\text{O}_2 \longrightarrow 2\text{NO} + 3/2\text{H}_2\text{O}$ | -226.51 | -239.87 |

Isothermal batch reactor data

- Reaction kinetics are most easily and inexpensively obtained in a small batch reactor.
 - A mixture of liquids in a beaker or flask on a hot plate or in a thermostatted water or sand bath.
 - A container with gases and heating appropriately.
- Analyzing the composition of the reactor versus time.
 - GC, LC, spectroscopic methods (IR, UV, ...), etc.
 - For gases in a constant volume batch reactor, the conversion may be determined by measuring the pressure change.

Fit data with a suitable rate expression (Essen's method)

When we have an irreversible reaction with a single reactant and power law kinetics,

- For first order reaction

$$r = \frac{dC_A}{dt} = -kC_A$$

$$\ln C_A - \ln C_{A0} = -kt$$

- For second order reaction

$$r = \frac{dC_A}{dt} = -kC_A^2$$

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt$$

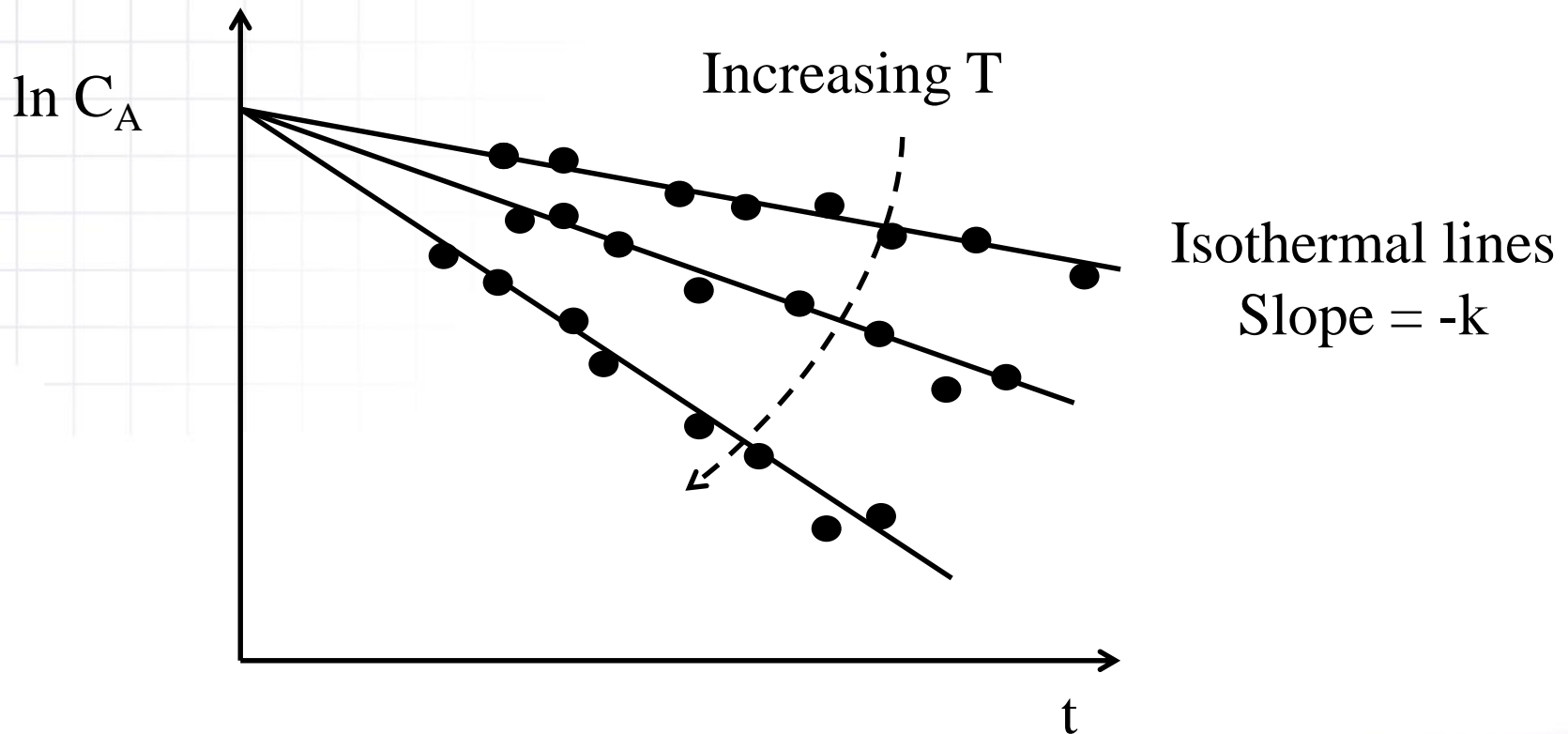
- For n order reaction ($n \neq 1$)

$$r = \frac{dC_A}{dt} = -kC_A^n$$

$$\frac{1}{-n+1} (C_A^{-n+1} - C_{A0}^{-n+1}) = kt$$

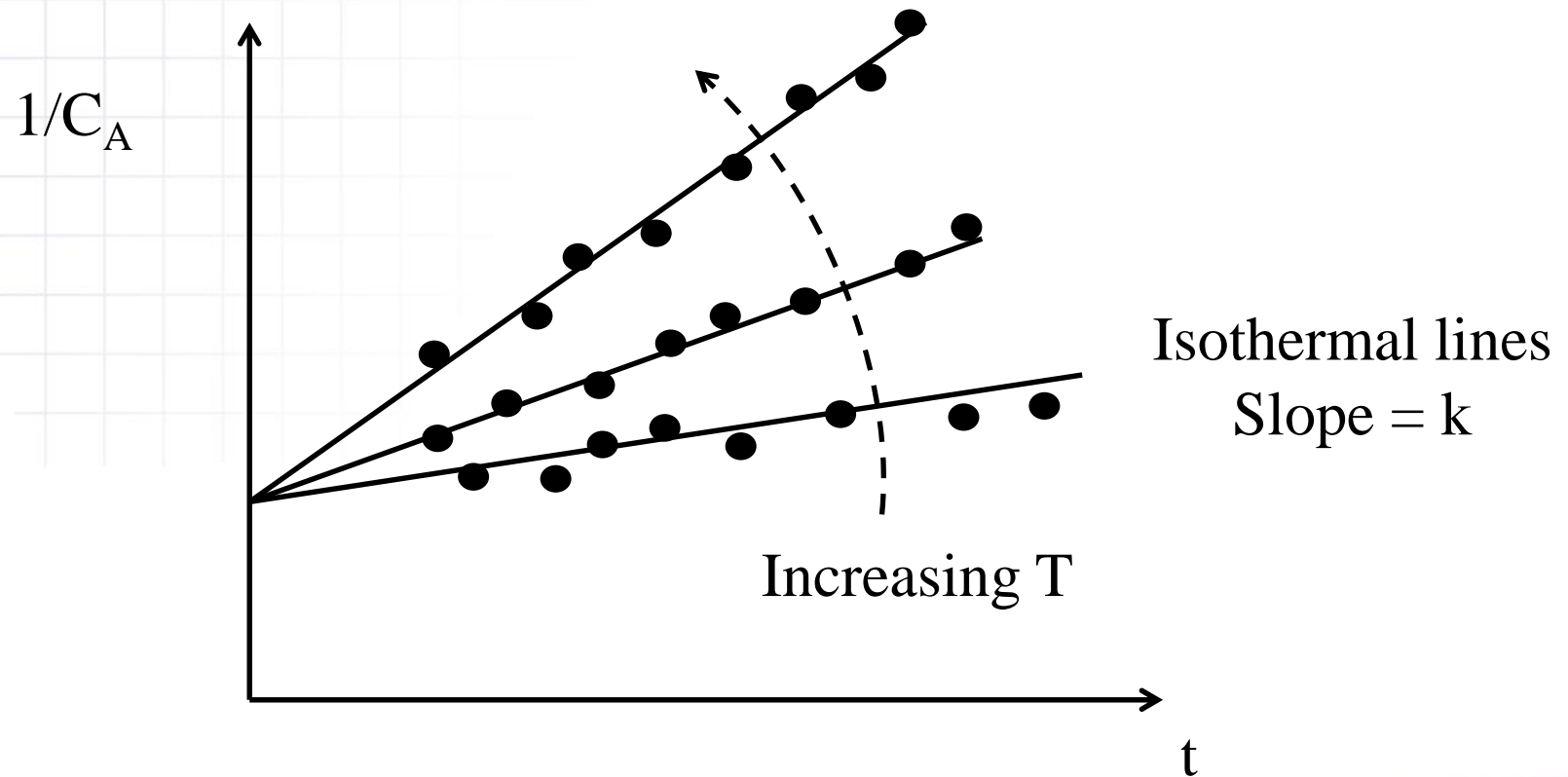
First order irreversible reaction

$$\ln C_A - \ln C_{A0} = -kt$$



Second order irreversible reaction

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt$$



Van't Hoff's method

It is not uncommon for more than one rate equation to fit the data within the experimental uncertainties. One should not infer that the rate equation is correct just because the data fits. One can easily be fooled into thinking that a reaction with a complex rate equation follows simple first or second order kinetics.

- For first order reaction, $k = \ln (C_{A0}/C_A)/t$
- For n order reaction ($n \neq 1$), $k_n = \frac{1}{-n+1} (C_A^{-n+1} - C_{A0}^{-n+1})/t$

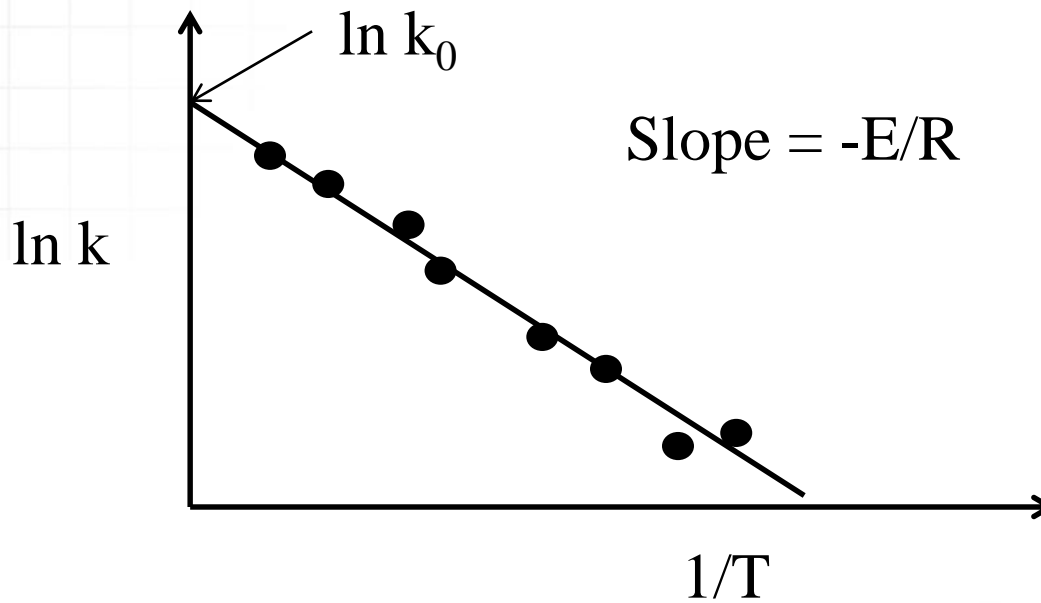
Van't Hoff asserted that it is important to check the results from Essen's method. Using the above equations to calculate k_n at various time and make a plot of k_n vs time. k_n should work out to be constant within experimental error. If k_n varies in any sort of systematic way, then the reaction is not really the accepted first or second order.

Temperature dependence

We expect the slopes k from the above plots should depend on T as

$$k(T) = k_0 \exp(-E/RT)$$

$$\ln k = \ln k_0 - E/RT$$



Multiple reactant species

- Consider a reaction:



The reaction rate data can be obtained by using a large excess of one component. For example, let $C_{B0} \gg C_{A0}$, so the C_B remains nearly constant. Thus, the rate becomes

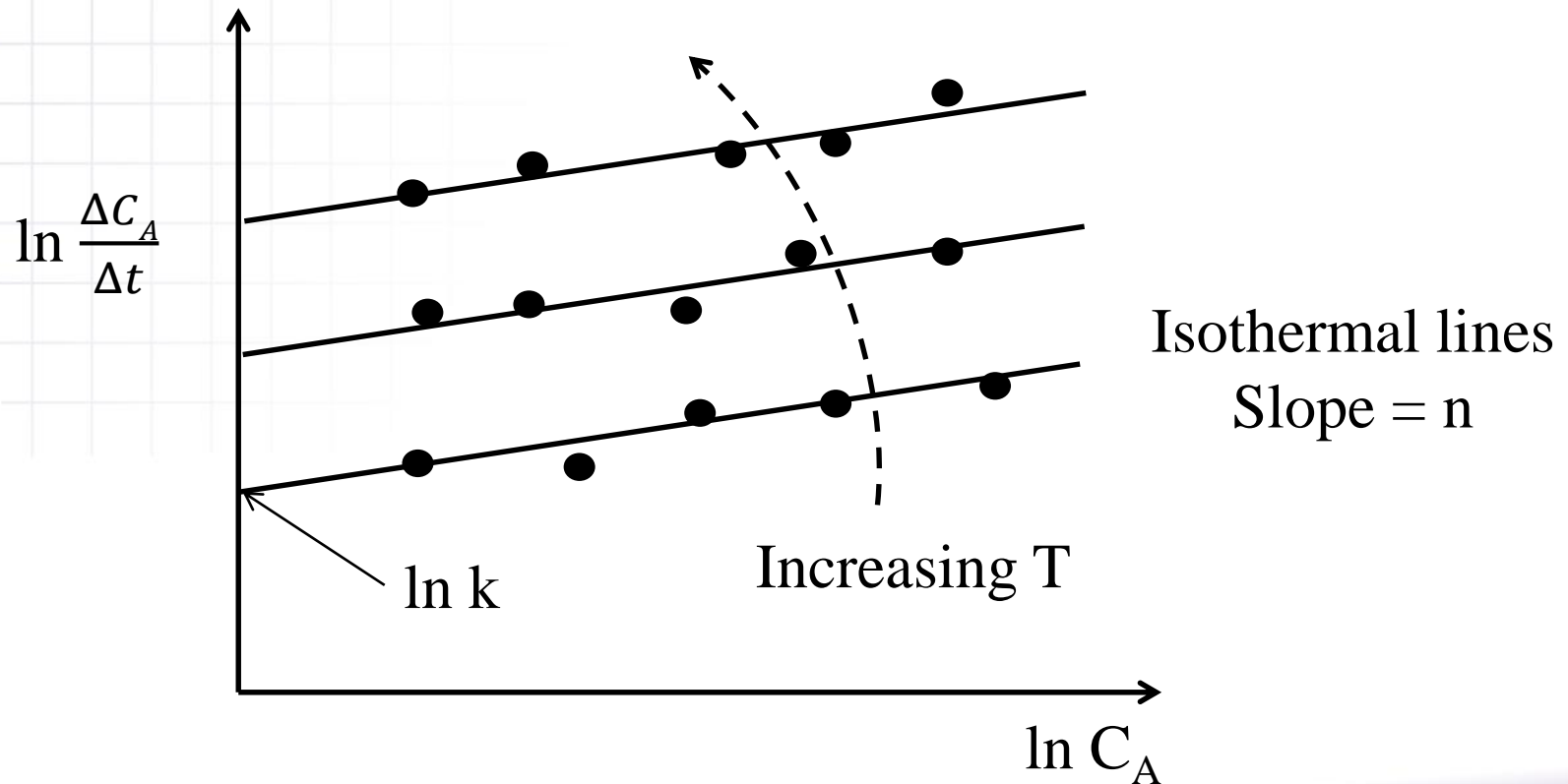
$$r = -kC_A C_{B0} = -(kC_{B0})C_A$$

A plot of C_A versus t would have a slope $-kC_{B0}$. One would repeat the experiment with $C_{A0} \gg C_{B0}$, where a plot of C_B versus t would have a slope $-kC_{A0}$.

Differential reactor data

- Concentration does not change much from the initial concentration

$$\frac{dC_A}{dt} = -kC_a^n \text{ can be written as } \ln \frac{\Delta C_A}{\Delta t} = \ln k + n \ln C_A$$



Determining exponents for a rate law from initial rates

If we are given data from two or more experiments at the same temperature with different concentrations of reactants and different rates we can determine the exponents in the differential rate law for the reaction as follows:

(1) Write the rate law with the coefficients as unknowns: n , m , etc.

$$r = kC_A^n C_B^m$$

(2) Take ratios of the experimental data that give different rates.

$$\frac{r_1}{r_2} = \frac{kC_{A1}^n C_{B1}^m}{kC_{A2}^n C_{B2}^m}$$

(3) Cancel common terms and solve for the exponent that does not cancel.

Example

| Experiment | C_A, M | C_B, M | $r, M/h$ |
|------------|----------|----------|----------|
| 1 | 0.50 | 0.50 | 1.2 |
| 2 | 1.0 | 0.50 | 4.8 |
| 3 | 2.0 | 1.0 | 38.4 |

Take ratios of data from experiments 1 and 2 that give different rates.

$$\frac{1.2}{4.8} = \frac{k0.5^n0.5^m}{k1.0^n0.5^m} \rightarrow n=2$$

Take ratios of data from experiments 1 and 3 that give different rates.

$$\frac{1.2}{38.4} = \frac{k0.5^20.5^m}{k2.0^21.0^m} \rightarrow m=1$$

So the rate law can be written

$$r = kC_A^2C_B$$

Direct vs indirect methods

Direct or differential methods

(Rate is directly measure as a function of concentrations)

Indirect or integral methods

(rate is determined by fitting measured concentrations into a theoretical expression)

Advantages

- Easy to fit data
- Get rate equation directly
- High confidence on rate equation

- Easier experiment
 - A few runs can provide important information
 - Suitable for all reactions
-

Disadvantages

- Difficult experiment
- Need many runs
- Not suitable for very fast or very slow reactions

- Hard to analyze data
 - Must infer rate equation
 - Low confidence on rate equation
-

Complications

- The data obtained by the above methods must be analyzed carefully to assess its accuracy and determine the statistical confidence (e.g. a least square analysis may be used).
- Sometimes it is difficult to maintain reactors strictly isothermal because all reactions liberate or absorb heat. These effects can be minimized by diluting reactants and using low temperatures, thus making reaction rates sufficiently slow that the system can be thermostatted accurately.
- One must be careful of necessary extrapolation to operating conditions.
- Reaction rate data is sometimes acquired in continuous reactors rather than batch reactors. The composition will not be a function of time after the reactor has come to steady state. One must wait until the reactor has come to steady state after any changes in feed or process conditions.

Continuous reactors

- It is common to follow batch experiments with a lab scale continuous reactor process to examine more properties of the reaction system.
- Continuous reactor use much more reactants, and often are operated day and night.
- The costs of running continuous processes are much higher than batch processes.
- Preliminary data on a process is often obtained using batch reactors by chemists; while a continuous process often need involvement of engineers.

Problem

- The half-life of a first-order reaction was found to be 10 min at a certain temperature. What is its rate constant?
- Solution:

$$k = -\ln(C_A/C_{A0})/t = -\ln(1/2)/600 = 0.693/600 = 0.00115 \text{ s}^{-1}$$

Solution

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