Updated: 4 September 2013

Print version

CEE 697K
ENVIRONMENTAL REACTION KINETICS

Lecture #2

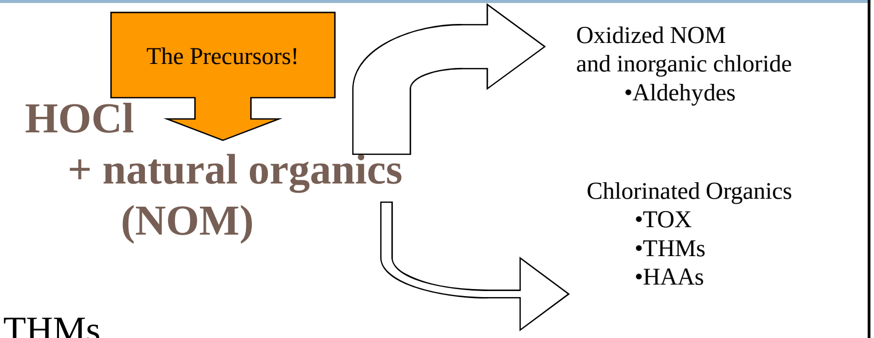
Rate Expressions: Bromide + Chlorine case study & lab project

Kumar & Margerum paper

David A. Reckhow

Introduction

Reactions with Chlorine



The Precursors!

HOCl

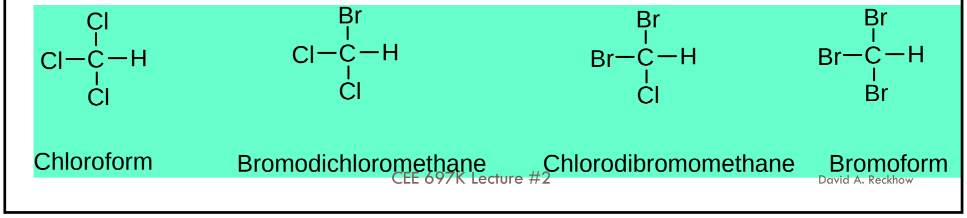
+ natural organics

(NOM)

Oxidized NOM
and inorganic chloride
- Aldehydes

Chlorinated Organics
- TOX
- THMs
- HAAs

The THMs



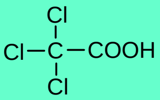
Chloroform

Bromodichloromethane

Chlorodibromomethane

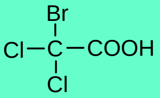
Bromoform

The Haloacetic Acids



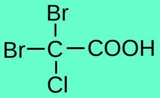
$\mathrm{Cl-\overset{Cl}{\underset{Cl}{C}}-COOH}$

Trichloroacetic Acid
(TCAA)



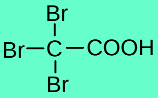
$\mathrm{Cl-\overset{Br}{\underset{Cl}{C}}-COOH}$

Bromodichloroacetic Acid



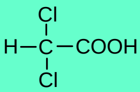
$\mathrm{Br-\overset{Br}{\underset{Cl}{C}}-COOH}$

Chlorodibromoacetic Acid



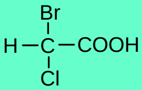
$\mathrm{Br-\overset{Br}{\underset{Br}{C}}-COOH}$

Tribromoacetic Acid



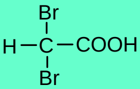
$\mathrm{H-\overset{Cl}{\underset{Cl}{C}}-COOH}$

Dichloroacetic Acid
(DCAA)



$\mathrm{H-\overset{Br}{\underset{Cl}{C}}-COOH}$

Bromochloroacetic Acid

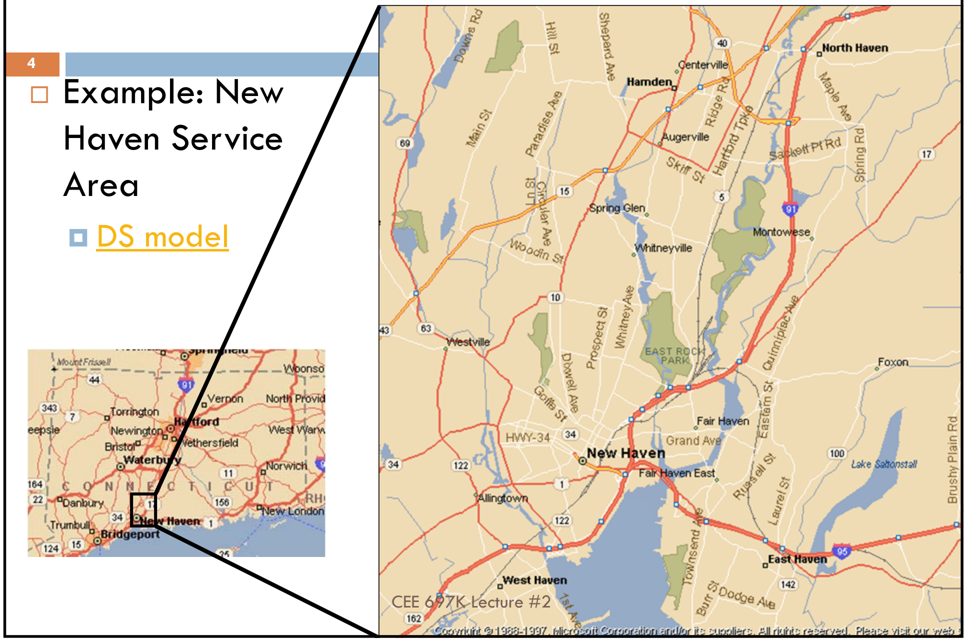


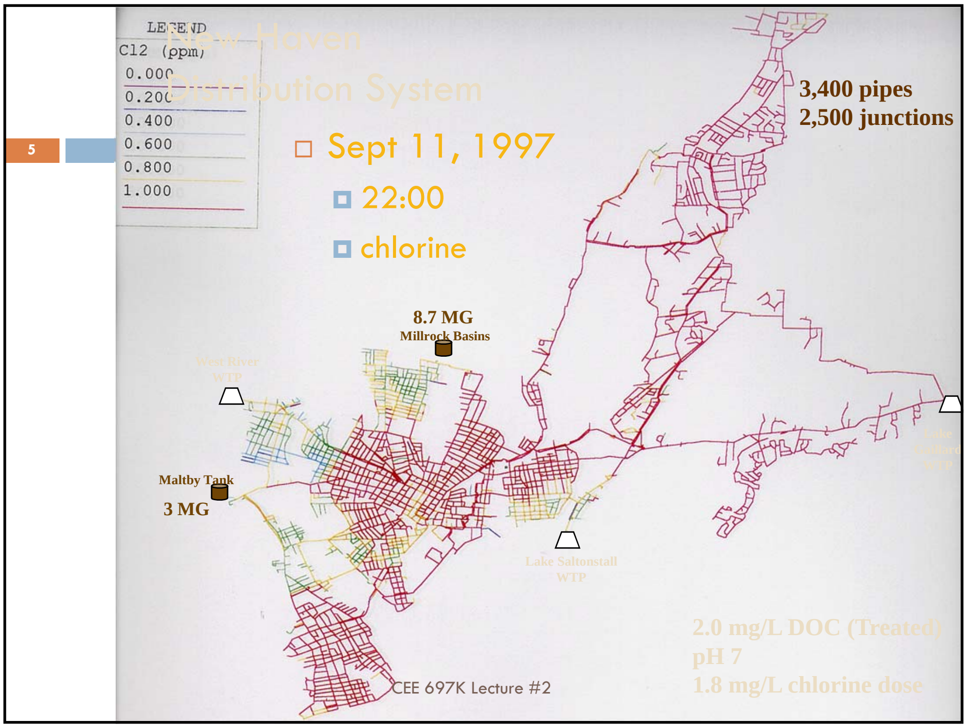
$\mathrm{H-\overset{Br}{\underset{Br}{C}}-COOH}$

Dibromoacetic Acid

Distribution: Variability within a single system

- Example: New Haven Service Area
  - DS model



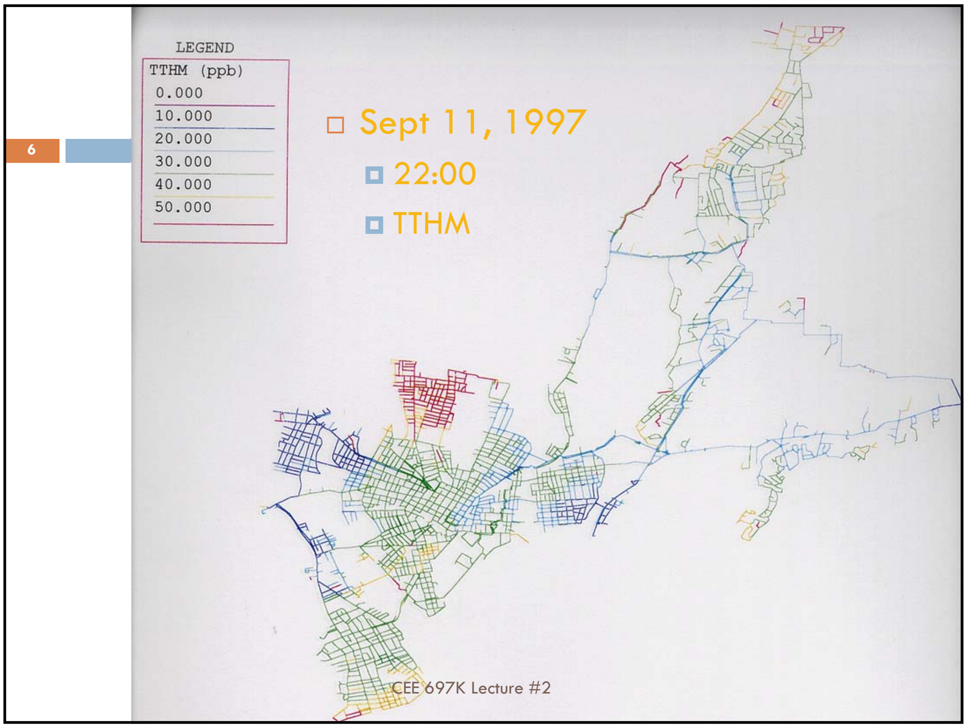


New Haven Distribution System

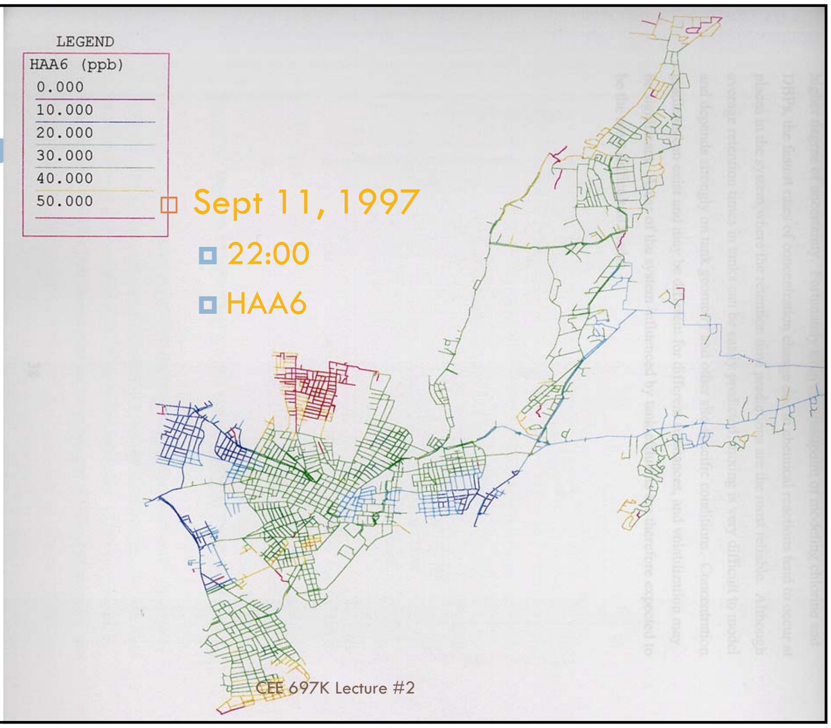
- Sept 11, 1997
  - 22:00
  - chlorine

3,400 pipes
2,500 junctions

2.0 mg/L DOC (Treated)
pH 7
1.8 mg/L chlorine dose



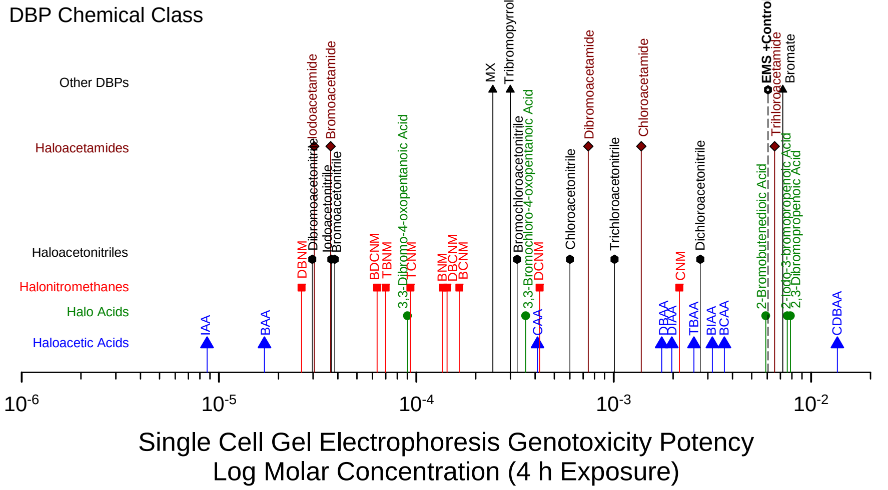
- Sept 11, 1997
  - 22:00
  - TTHM



- Sept 11, 1997
  - 22:00
  - HAA6

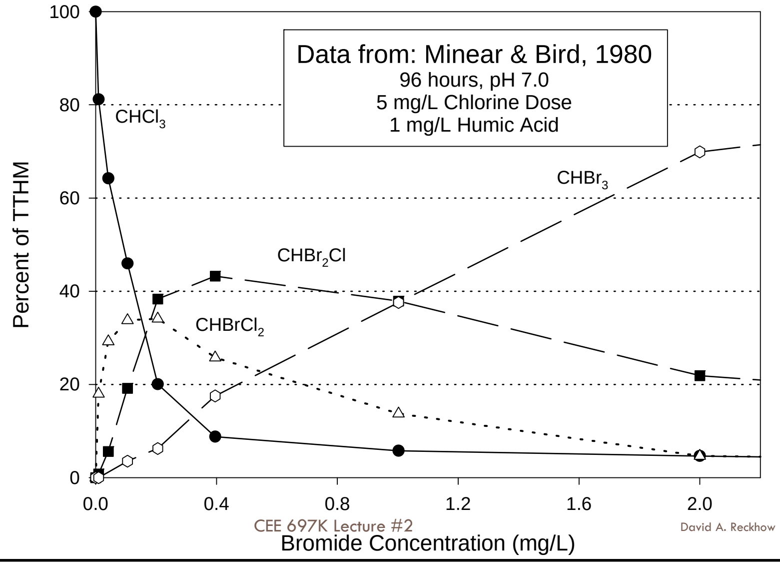
Genotoxicity

- Work of Michael Plewa
  - Univ. of Illinois

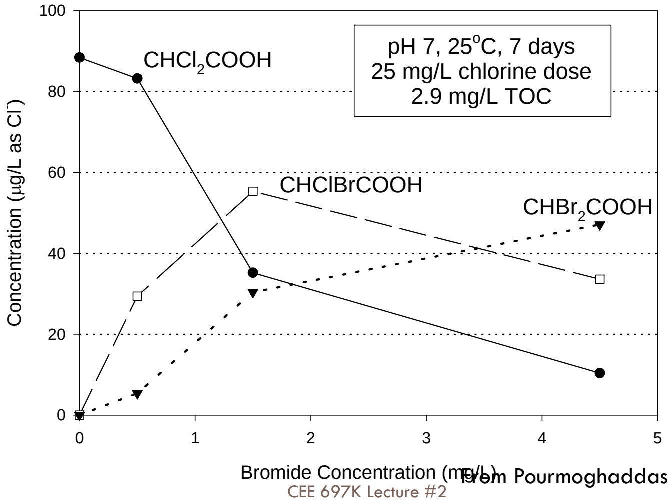


Not Genotoxic: DCAA, TCAA, BDCAA, Dichloroacetamide, 3,3-Dibromopropenoic Acid, 3-Iodo-3-bromopropenoic Acid, 2,3,3,Tribromopropenoic Acid

Bromide: THM Formation

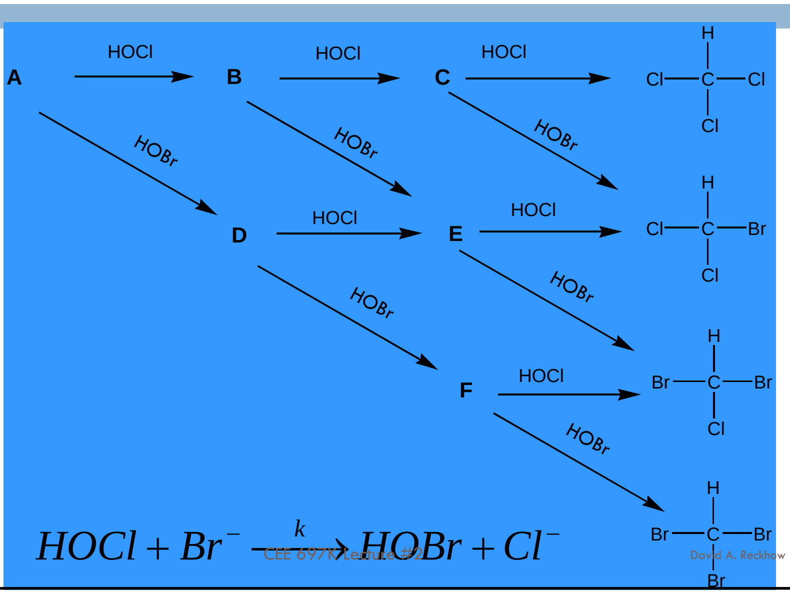


Impact of Bromide on DHAA Formation



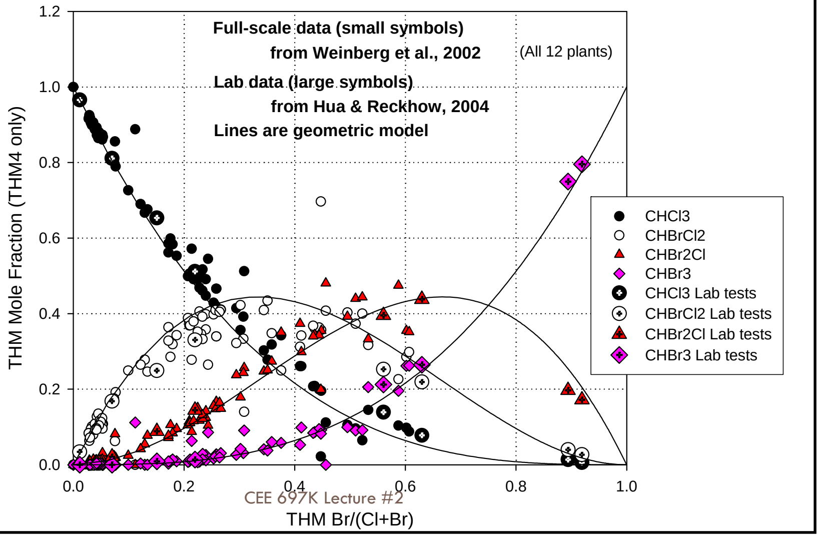
From Pourmoghaddas, 1990

Formation of Brominated THMs



$$HOCl + Br^{-} \xrightarrow{k} HOBr + Cl^{-}$$

Bromo speciation



Full-scale data (small symbols) from Weinberg et al., 2002

(All 12 plants)

Lab data (large symbols) from Hua & Reckhow, 2004

Lines are geometric model

Case study: chlorine + bromide

- Observed reaction $HOCl + Br^{-} \xrightarrow{k_2} HOBr + Cl^{-}$
  - Nucleophilic attack of bromide on oxygen in hypochlorous acid
    - $k_2 = 2.95 \times 10^{3}\ M^{-1}s^{-1}$ at 25°C
      - Note that HOCl deprotonates at elevated pHs
      - From Farkas et al., 1949
  - Transfer of Cl^{+} to form intermediate (BrCl)

$$HA + HOCl + Br^{-} \xrightarrow{k_3} A^{-} + H_2O + BrCl$$

$$BrCl + Br^{-} \xleftrightarrow{fast} Br_2 + Cl^{-} \qquad Br_2 + Br^{-} \xleftrightarrow{fast} Br_3^{-}$$

- From Kumar & Margerum, 1987

Background

- Absorbance for monitoring reaction
- Known equilibria

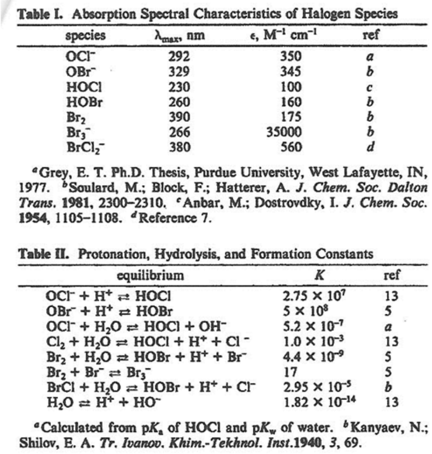


Table I. Absorption Spectral Characteristics of Halogen Species

species	λ_{max}, nm	ϵ, $M^{-1}\ cm^{-1}$	ref
OCl^{-}	292	350	*a*
OBr^{-}	329	345	*b*
HOCl	230	100	*c*
HOBr	260	160	*b*
Br_2	390	175	*b*
Br_3^{-}	266	35000	*b*
$BrCl_2^{-}$	380	560	*d*

[a] Grey, E. T. Ph.D. Thesis, Purdue University, West Lafayette, IN, 1977. [b] Soulard, M.; Block, F.; Hatterer, A. *J. Chem. Soc. Dalton Trans.* **1981**, 2300–2310. [c] Anbar, M.; Dostrovdky, I. *J. Chem. Soc.* **1954**, 1105–1108. [d] Reference 7.

Table II. Protonation, Hydrolysis, and Formation Constants

equilibrium	*K*	ref
$OCl^{-} + H^{+} \rightleftarrows HOCl$	2.75×10^{7}	13
$OBr^{-} + H^{+} \rightleftarrows HOBr$	5×10^{8}	5
$OCl^{-} + H_2O \rightleftarrows HOCl + OH^{-}$	5.2×10^{-7}	*a*
$Cl_2 + H_2O \rightleftarrows HOCl + H^{+} + Cl^{-}$	1.0×10^{-3}	13
$Br_2 + H_2O \rightleftarrows HOBr + H^{+} + Br^{-}$	4.4×10^{-9}	5
$Br_2 + Br^{-} \rightleftarrows Br_3^{-}$	17	5
$BrCl + H_2O \rightleftarrows HOBr + H^{+} + Cl^{-}$	2.95×10^{-5}	*b*
$H_2O \rightleftarrows H^{+} + HO^{-}$	1.82×10^{-14}	13

[a] Calculated from pK_a of HOCl and pK_w of water. [b] Kanyaev, N.; Shilov, E. A. *Tr. Ivanov. Khim.-Tekhnol. Inst.* **1940**, *3*, 69.

Alkaline Experiments

- Pseudo-1st order
  - Bromide in great excess
- Slow reactions
  - Could be monitored directly by conventional UV spectrophotometer
    - 292 nm peak for hypochlorite (OCl^-)
  - Followed for 4 half-lives
    - Complete from: 1.1 sec – 4 hr
  - Plot $\ln(A_t - A_\infty)$ vs time
    - Slope is k_{obs}

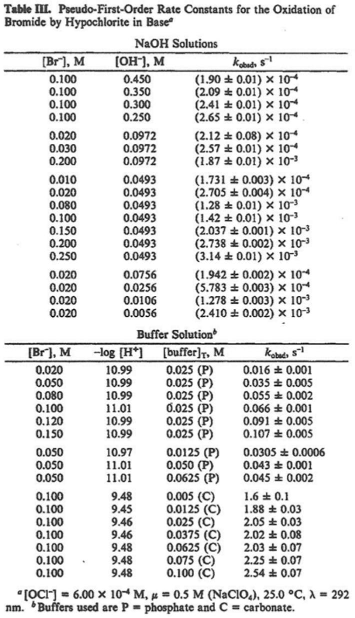


Table III. Pseudo-First-Order Rate Constants for the Oxidation of Bromide by Hypochlorite in Base[a]

NaOH Solutions

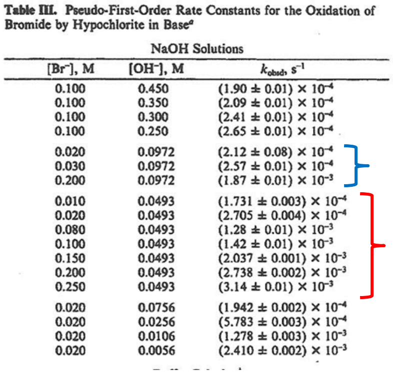
$[Br^-]$, M	$[OH^-]$, M	k_{obsd}, s^{-1}
0.100	0.450	$(1.90 \pm 0.01) \times 10^{-4}$
0.100	0.350	$(2.09 \pm 0.01) \times 10^{-4}$
0.100	0.300	$(2.41 \pm 0.01) \times 10^{-4}$
0.100	0.250	$(2.65 \pm 0.01) \times 10^{-4}$
0.020	0.0972	$(2.12 \pm 0.08) \times 10^{-4}$
0.030	0.0972	$(2.57 \pm 0.01) \times 10^{-4}$
0.200	0.0972	$(1.87 \pm 0.01) \times 10^{-3}$
0.010	0.0493	$(1.731 \pm 0.003) \times 10^{-4}$
0.020	0.0493	$(2.705 \pm 0.004) \times 10^{-4}$
0.080	0.0493	$(1.28 \pm 0.01) \times 10^{-3}$
0.100	0.0493	$(1.42 \pm 0.01) \times 10^{-3}$
0.150	0.0493	$(2.037 \pm 0.001) \times 10^{-3}$
0.200	0.0493	$(2.738 \pm 0.002) \times 10^{-3}$
0.250	0.0493	$(3.14 \pm 0.01) \times 10^{-3}$
0.020	0.0756	$(1.942 \pm 0.002) \times 10^{-4}$
0.020	0.0256	$(5.783 \pm 0.003) \times 10^{-4}$
0.020	0.0106	$(1.278 \pm 0.003) \times 10^{-3}$
0.020	0.0056	$(2.410 \pm 0.002) \times 10^{-3}$

Buffer Solution[b]

$[Br^-]$, M	$-\log [H^+]$	$[buffer]_T$, M	k_{obsd}, s^{-1}
0.020	10.99	0.025 (P)	0.016 ± 0.001
0.050	10.99	0.025 (P)	0.035 ± 0.005
0.080	10.99	0.025 (P)	0.055 ± 0.002
0.100	11.01	0.025 (P)	0.066 ± 0.001
0.120	10.99	0.025 (P)	0.091 ± 0.005
0.150	10.99	0.025 (P)	0.107 ± 0.005
0.050	10.97	0.0125 (P)	0.0305 ± 0.0006
0.050	11.01	0.050 (P)	0.043 ± 0.001
0.050	11.01	0.0625 (P)	0.045 ± 0.002
0.100	9.48	0.005 (C)	1.6 ± 0.1
0.100	9.45	0.0125 (C)	1.88 ± 0.03
0.100	9.46	0.025 (C)	2.05 ± 0.03
0.100	9.46	0.0375 (C)	2.02 ± 0.08
0.100	9.48	0.0625 (C)	2.03 ± 0.07
0.100	9.48	0.075 (C)	2.25 ± 0.07
0.100	9.48	0.100 (C)	2.54 ± 0.07

[a] $[OCl^-] = 6.00 \times 10^{-4}$ M, $\mu = 0.5$ M ($NaClO_4$), 25.0 °C, $\lambda = 292$ nm. [b] Buffers used are P = phosphate and C = carbonate.

K_{obs} is a linear function of Bromide



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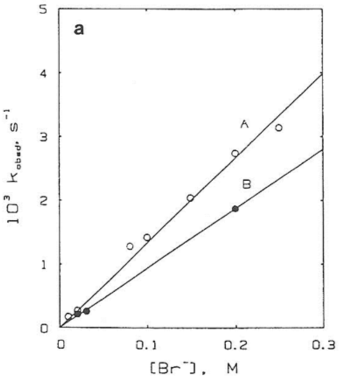
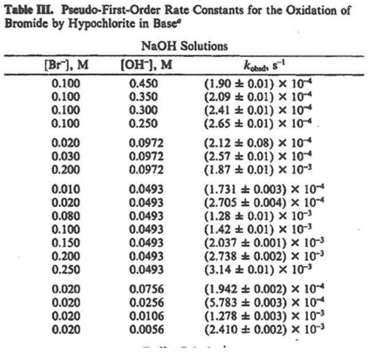


pH dependency



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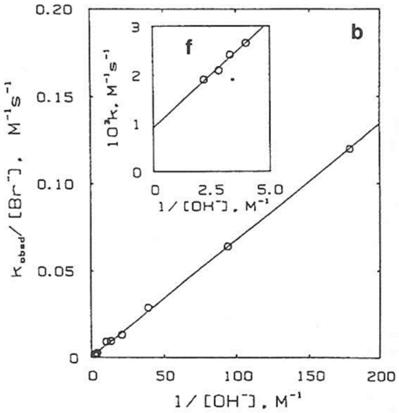

Overall pH dependence

- How to explain pH effect on 2nd order rate constant?
  - See also, Brezonik, pg 230; figure 4-20

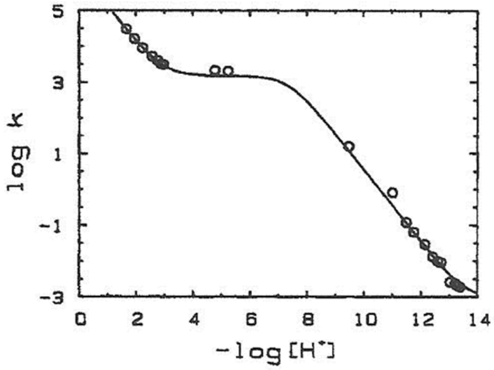

Figure 7. Dependence of the second-order rate constant (in terms of $[OCl^-]_T$ and $[Br^-]$) on the acidity (without buffer catalysis effects).

Buffer Tests

- ☐ Low pH →
- ☐ High pH ↓

Buffer Solution[b]

$[Br^-]$, M	$-\log [H^+]$	$[buffer]_T$, M	k_{obsd}, s^{-1}
0.020	10.99	0.025 (P)	0.016 ± 0.001
0.050	10.99	0.025 (P)	0.035 ± 0.005
0.080	10.99	0.025 (P)	0.055 ± 0.002
0.100	11.01	0.025 (P)	0.066 ± 0.001
0.120	10.99	0.025 (P)	0.091 ± 0.005
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0.050	11.01	0.050 (P)	0.043 ± 0.001
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0.100	9.46	0.0375 (C)	2.02 ± 0.08
0.100	9.48	0.0625 (C)	2.03 ± 0.07
0.100	9.48	0.075 (C)	2.25 ± 0.07
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[a] $[OCl^-] = 6.00 \times 10^{-4}$ M, $\mu = 0.5$ M ($NaClO_4$), 25.0 °C, $\lambda = 292$ nm. [b] Buffers used are P = phosphate and C = carbonate.

Table IV. Pseudo-First-Order Rate Constants for the Oxidation of Bromide by Hypochlorous Acid[a]

Buffer Solutions[b]

$[Br^-]$, M	$-\log [H^+]$	$[buffer]_T$, M	k_{obsd}, s^{-1}
0.010	5.23	0.05 (A)	24.7 ± 0.4
0.020	5.22	0.05 (A)	46.1 ± 0.5
0.050	5.22	0.05 (A)	115 ± 4[c]
0.100	5.30	0.05 (A)	245 ± 4[c]
0.0050	4.78	0.01 (A)	10.83 ± 0.07
0.0050	4.78	0.02 (A)	11.27 ± 0.13
0.0050	4.78	0.05 (A)	12.58 ± 0.05
0.0050	4.78	0.10 (A)	14.65 ± 0.06
0.0050	4.78	0.20 (A)	18.8 ± 0.8
0.0050	2.90	0.01 (C)	16.6 ± 0.2
0.0050	2.87	0.025 (C)	19.44 ± 0.08
0.0050	2.85	0.050 (C)	22.2 ± 0.5
0.0050	2.84	0.100 (C)	27.8 ± 0.4
0.0050	2.83	0.125 (C)	30.0 ± 0.4

Perchloric Acid Solutions

$[Br^-]$, M	$10^3[H^+]$, M	k_{obsd}, s^{-1}
0.0020	1.063	6.33 ± 0.05
0.003	1.063	9.75 ± 0.06
0.004	1.063	12.7 ± 0.2
0.005	1.063	16.3 ± 0.3
0.010	1.063	31.7 ± 0.4
0.020	1.063	63.2 ± 0.7
0.005	1.59	19.6 ± 0.2
0.005	2.66	26.4 ± 0.3
0.005	5.84	45.1 ± 0.4
0.005	11.16	81 ± 2[c]
0.005	21.79	154 ± 2[c]

[a] $[HOCl] = (0.5–6.00) \times 10^{-4}$ M, $\mu = 0.5$ M ($NaClO_4$), 25.0 °C, λ = 266 or 392 nm. [b] Buffers used are A = acetic acid and C = chloroacetic acid. [c] Rate constants are corrected for mixing.[12]

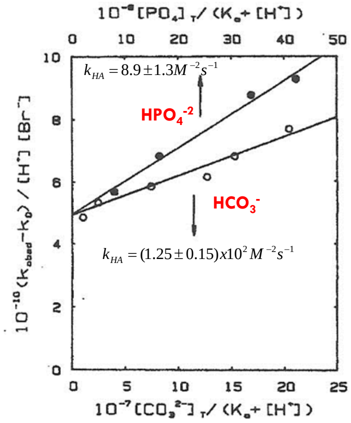
Buffer Effect

- ☐ Proposed dependence on HA

$$k_{obs} = \left(k_0 + k_H[H^+] + k_{HA}[HA]\right)[Br^-]$$

$$[HA] = \alpha_0 C_T = \frac{1}{\frac{K_a}{[H^+]}+1} C_T = \boxed{\frac{[H^+]C_T}{K_a+[H^+]}}$$

$$\frac{\left(\frac{k_{obs}}{[Br^-]}\right) - k_0}{[H^+]} = k_H + k_{HA}\left(\frac{[buffer]_T}{K_a+[H^+]}\right)$$



- High pH only

$$k_{obs} = \left(k_0 + k_H[H^+] + k_{HA}[HA]\right)[Br^-]$$

$$-\frac{d[OCl^-]}{dt} = \left(k_0 + k_H[H^+] + k_{HA}[HA]\right)[OCl^-][Br^-]$$

- More generally

$$-\frac{d[Cl(+I)]}{dt} = \left(k_0[OCl^-] + k_{HOCl}[HOCl] + k_{HA}[HA][OCl^-]\right)[Br^-]$$

Acidic Experiments

- Pseudo-1st order
  - Bromide in great excess
- Fast reactions
  - Required high-speed setup
    - Stopped-flow spectrophotometer
  - Could monitor 2° product
    - 266 nm peak for tribromide (Br_3^-)
  - Followed for 4 half-lives
    - Complete from 0.40-0.01 sec
  - Plot $\ln(A_t - A_\infty)$ vs time
    - Slope is k_{obs}

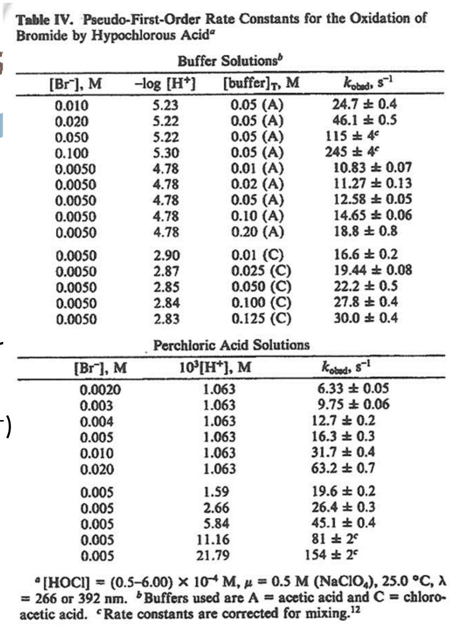


Table IV. Pseudo-First-Order Rate Constants for the Oxidation of Bromide by Hypochlorous Acid[a]

Buffer Solutions[b]

$[Br^-]$, M	$-\log [H^+]$	$[\text{buffer}]_T$, M	k_{obsd}, s^{-1}
0.010	5.23	0.05 (A)	24.7 ± 0.4
0.020	5.22	0.05 (A)	46.1 ± 0.5
0.050	5.22	0.05 (A)	115 ± 4[c]
0.100	5.30	0.05 (A)	245 ± 4[c]
0.0050	4.78	0.01 (A)	10.83 ± 0.07
0.0050	4.78	0.02 (A)	11.27 ± 0.13
0.0050	4.78	0.05 (A)	12.58 ± 0.05
0.0050	4.78	0.10 (A)	14.65 ± 0.06
0.0050	4.78	0.20 (A)	18.8 ± 0.8
0.0050	2.90	0.01 (C)	16.6 ± 0.2
0.0050	2.87	0.025 (C)	19.44 ± 0.08
0.0050	2.85	0.050 (C)	22.2 ± 0.5
0.0050	2.84	0.100 (C)	27.8 ± 0.4
0.0050	2.83	0.125 (C)	30.0 ± 0.4

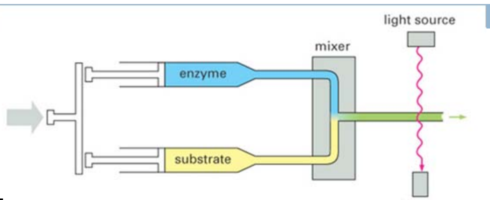
Perchloric Acid Solutions

$[Br^-]$, M	$10^3[H^+]$, M	k_{obsd}, s^{-1}
0.0020	1.063	6.33 ± 0.05
0.003	1.063	9.75 ± 0.06
0.004	1.063	12.7 ± 0.2
0.005	1.063	16.3 ± 0.3
0.010	1.063	31.7 ± 0.4
0.020	1.063	63.2 ± 0.7
0.005	1.59	19.6 ± 0.2
0.005	2.66	26.4 ± 0.3
0.005	5.84	45.1 ± 0.4
0.005	11.16	81 ± 2[c]
0.005	21.79	154 ± 2[c]

[a] $[HOCl] = (0.5\text{–}6.00) \times 10^{-4}$ M, $\mu = 0.5$ M ($NaClO_4$), 25.0 °C, $\lambda = 266$ or 392 nm. [b] Buffers used are A = acetic acid and C = chloroacetic acid. [c] Rate constants are corrected for mixing.[12]

Stopped-flow

- ☐ Principle



- ☐ Commercial instruments

- ☐ Limitations
  - Correct for slow mixing speed (k_m)
    - For Durrum instrument: $k_m = 1700\ s^{-1}$

$$k_{obs} = \frac{k'_{obs}}{\left[1-\left(k'_{obs}/k_m\right)\right]}$$

K_{obs} is still linear with Br-

- ☐ No difference in mechanism?

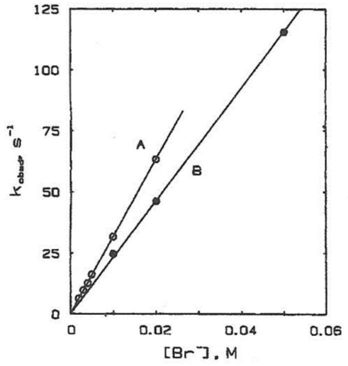


Figure 4. Pseudo-first-order rate constants (25.0 °C, $\mu = 0.50$) for the reaction of HOCl and Br^-: (A) $[H^+] = 1.063 \times 10^{-3}$ M; (B) $-\log [H^+] = 5.22$ (0.05 M acetate buffer).

Acidic data: impact of acids

- General and specific acid

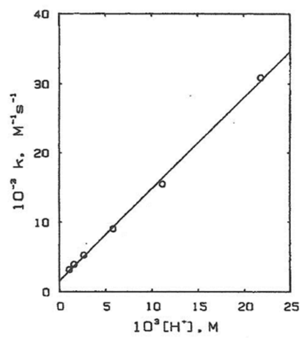


Figure 5. Dependence of the second-order rate constant (HOCl + Br⁻) on $HClO_4$ concentration.

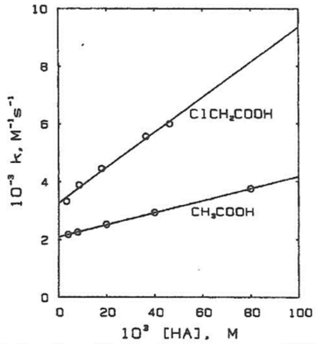
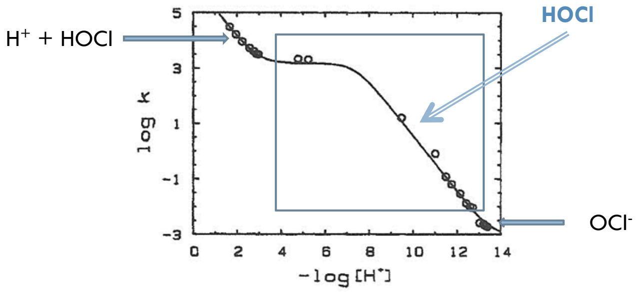


Figure 6. Dependence of the second-order rate constant (HOCl + Br⁻) on the concentration of general acids.

Overall pH dependence

- Three effective zones
  - See also, Brezonik, pg 230; figure 4-20



H^+ + HOCl

HOCl

OCl^-

Figure 7. Dependence of the second-order rate constant (in terms of $[OCl^-]_T$ and $[Br^-]$) on the acidity (without buffer catalysis effects).

Catalysis: comparison with pKa

- Bronsted catalysis

$$k_{HA} = G_A (K_a)^{\alpha}$$

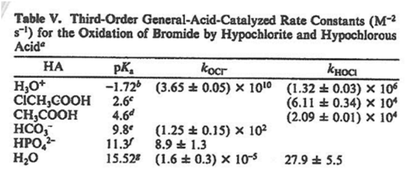


Table V. Third-Order General-Acid-Catalyzed Rate Constants (M^{-2} s^{-1}) for the Oxidation of Bromide by Hypochlorite and Hypochlorous Acid[a]

HA	pK_a	k_{OCl^-}	k_{HOCl}
H_3O^+	-1.72^b	$(3.65 \pm 0.05) \times 10^{10}$	$(1.32 \pm 0.03) \times 10^6$
$ClCH_3COOH$	2.6^c		$(6.11 \pm 0.34) \times 10^4$
CH_3COOH	4.6^d		$(2.09 \pm 0.01) \times 10^4$
HCO_3^-	9.8^e	$(1.25 \pm 0.15) \times 10^2$	
HPO_4^{2-}	11.3^f	8.9 ± 1.3	
H_2O	15.52^g	$(1.6 \pm 0.3) \times 10^{-5}$	27.9 ± 5.5

$\alpha = 0.75$ $\alpha = 0.27$

  - Indicates that HA engages in greater donation of proton to OCl^- than to HOCl

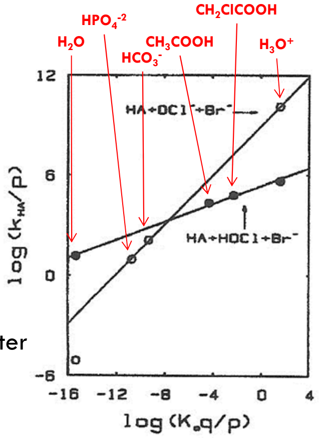
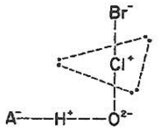


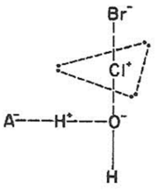
Figure 8. Brønsted plots for the general-acid-assisted reactions of OCl^- and Br^- and of HOCl and Br^-.

Mechanisms

- Proposed mechanism

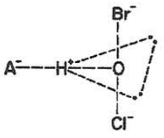


I

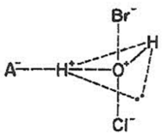


II

- Alternative
  - Less likely



III



IV

Temperature: Arrhenius Equation

- Arrhenius Equation

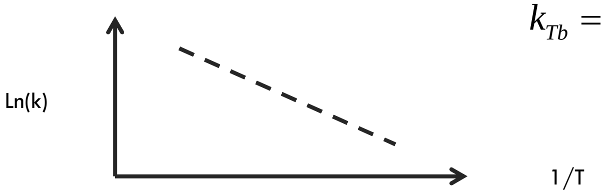
$$k = Ae^{-E_a/RT}$$

  - Where R is the universal gas constant $R = 8.3145\frac{J}{M\,^{o}K}$
- Transforms to:

$$Ln(k_T) = Ln(A) - \left(\frac{E_a}{R}\right)\frac{1}{T}$$

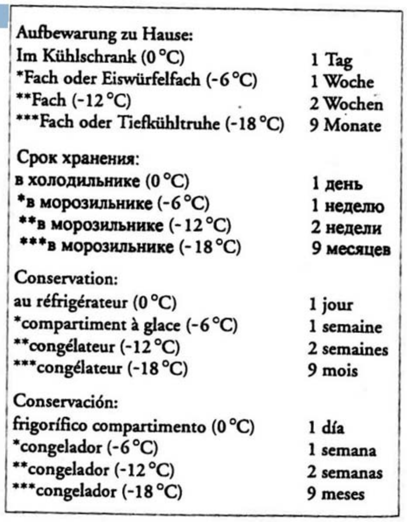
Or:

$$k_{Tb} = k_{Ta}e^{-\frac{E_a}{R}\left(\frac{1}{T_b}-\frac{1}{T_a}\right)}$$



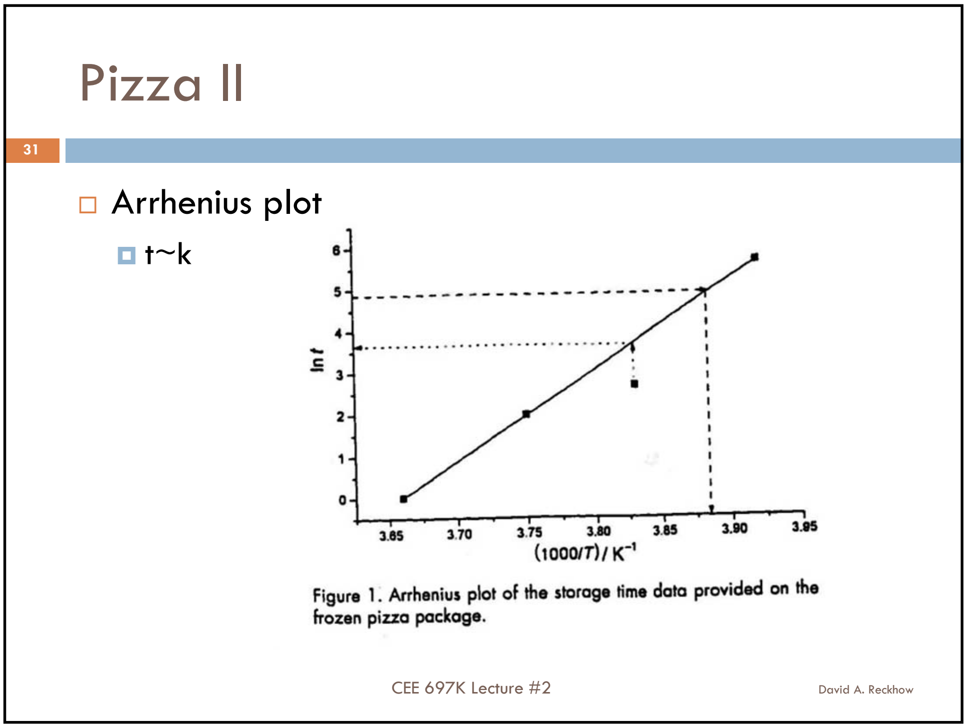
Pizza Kinetics

- Leenson, 1999
  - What are the kinetics of pizza spoilage?
  - Do they conform to Arrhenius?



Aufbewarung zu Hause:	
Im Kühlschrank (0 °C)	1 Tag
*Fach oder Eiswürfelfach (-6 °C)	1 Woche
**Fach (-12 °C)	2 Wochen
***Fach oder Tiefkühltruhe (-18 °C)	9 Monate
Срок хранения:	
в холодильнике (0 °C)	1 день
*в морозильнике (-6 °C)	1 неделю
**в морозильнике (-12 °C)	2 недели
***в морозильнике (-18 °C)	9 месяцев
Conservation:	
au réfrigérateur (0 °C)	1 jour
*compartiment à glace (-6 °C)	1 semaine
**congélateur (-12 °C)	2 semaines
***congélateur (-18 °C)	9 mois
Conservación:	
frigorífico compartimento (0 °C)	1 día
*congelador (-6 °C)	1 semana
**congelador (-12 °C)	2 semanas
***congelador (-18 °C)	9 meses

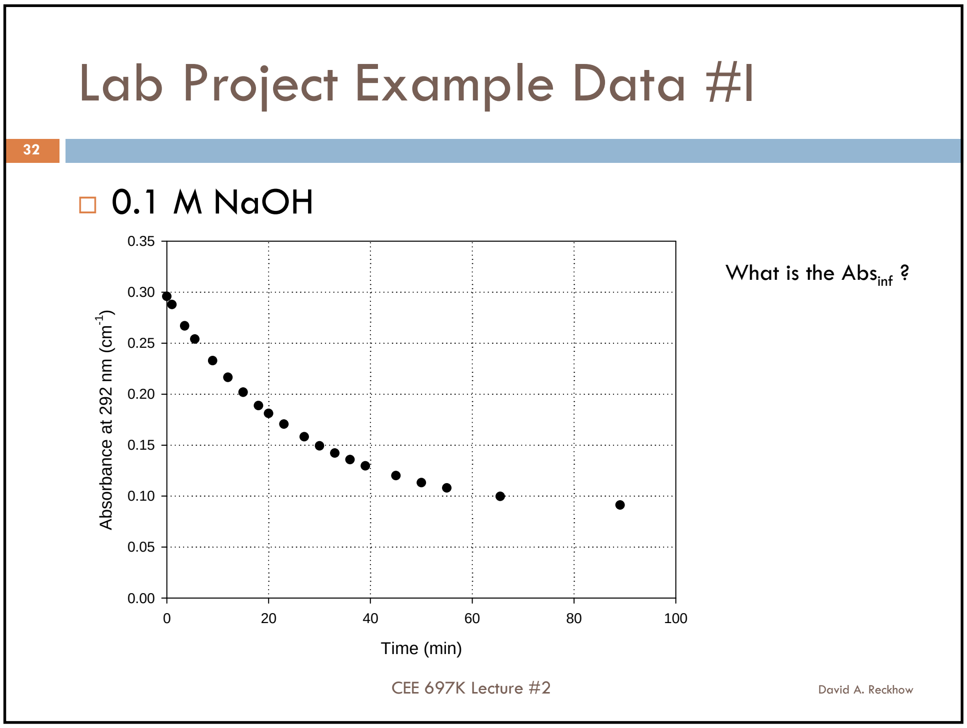
J. Chem Ed., 76:4:504-505



Pizza II

- Arrhenius plot
  - t~k

Figure 1. Arrhenius plot of the storage time data provided on the frozen pizza package.



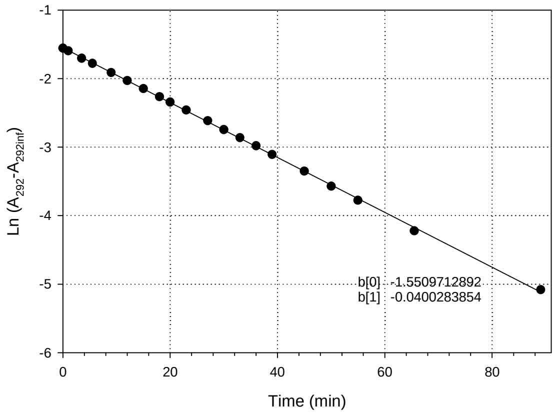
Lab Project Example Data #I

- 0.1 M NaOH

What is the $\mathrm{Abs}_{\mathrm{inf}}$?

Lab Project Example Data #II

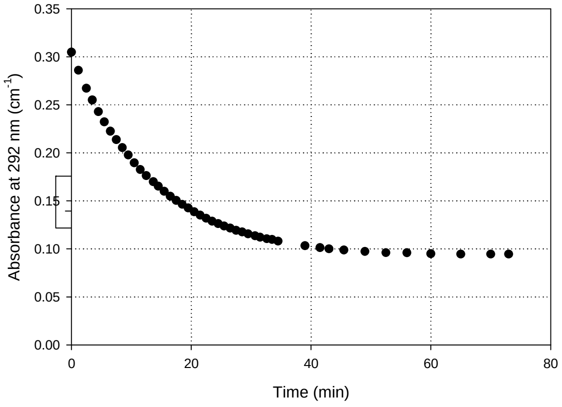
- 0.1 M NaOH



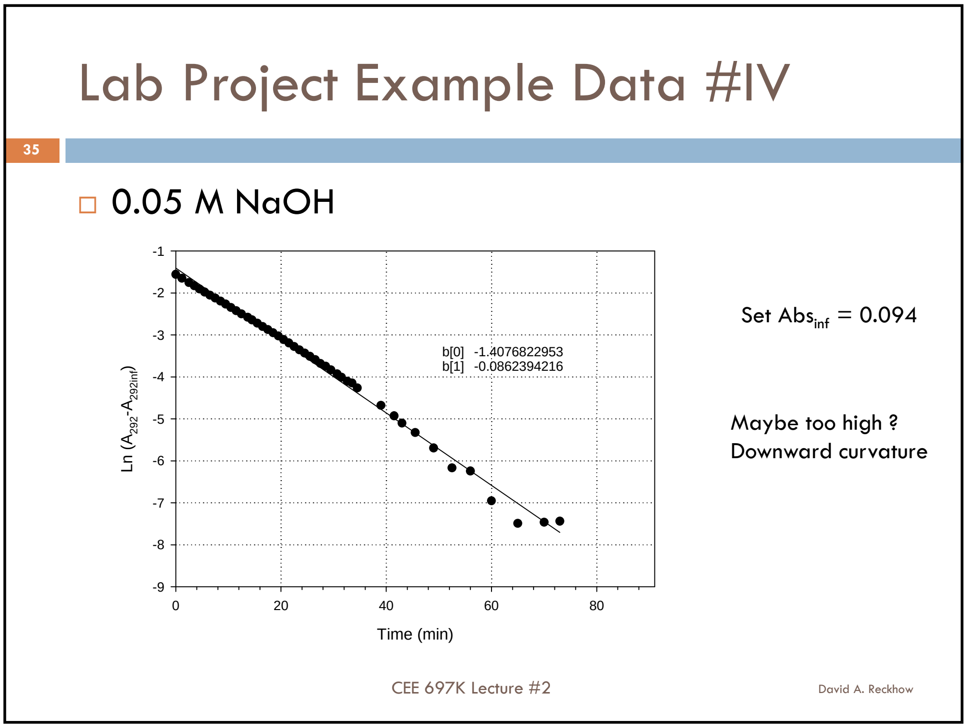
Set Abs_{inf} = 0.085

Lab Project Example Data #III

- 0.05 M NaOH



Set Abs_{inf} = ?

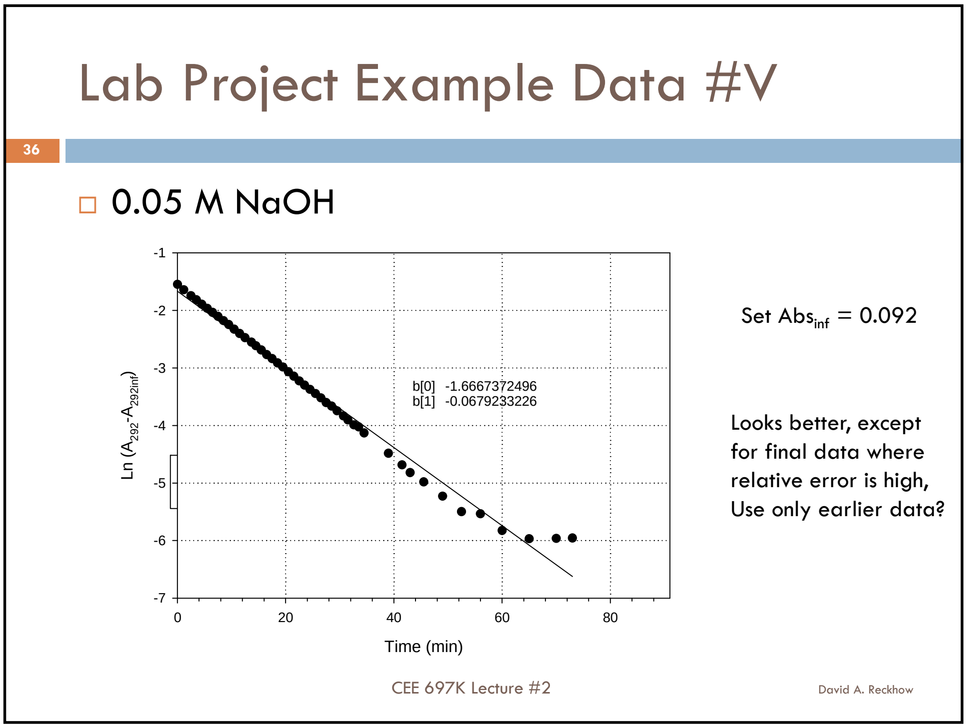


Lab Project Example Data #IV

- 0.05 M NaOH

Set Abs_{inf} = 0.094

Maybe too high ?
Downward curvature



Lab Project Example Data #V

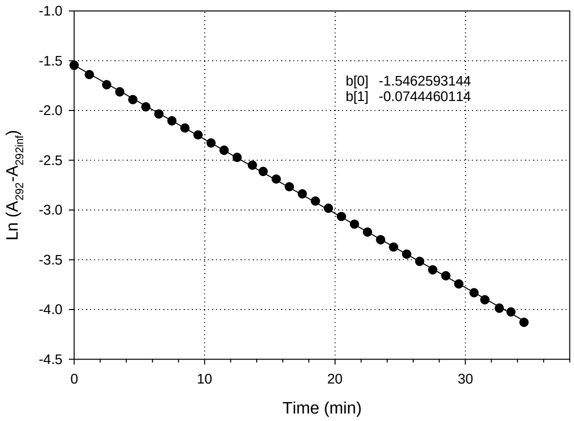
- 0.05 M NaOH

Set Abs_{inf} = 0.092

Looks better, except for final data where relative error is high, Use only earlier data?

Lab Project Example Data #VI

- ☐ 0.05 M NaOH



Set Abs_{inf} = 0.092

Using only earlier data where relative error is low,
Better linearity and estimate of k_{obs}?

Related systems

Table VI. Third-order Rate Constants for the Oxidation of Halides by Hypochlorite and by Hypohalous Acids

reactants	k, $M^{-2}\ s^{-1}$	ref
$H^+ + OCl^- + Br^-$	3.65×10^{10}	*a*
$H^+ + OCl^- + I^-$	4.4×10^{15}	*b*
$H^+ + HOCl + Cl^-$	2.8×10^{4}	*c*
$H^+ + HOCl + Br^-$	1.3×10^{6}	*a*
$H^+ + HOBr + Br^-$	1.6×10^{10}	*d*
$H^+ + HOI + I^-$	4.4×10^{12}	*d*

[a] This work. [b] Reference 2. [c] Reference 13. [d] Reference 5.

$$H_2O_2 + Br^- \xrightarrow{2.3 \times 10^{-5}\ M^{-1}\ s^{-1}} OH^- + HOBr \qquad (22)$$

$$H^+ + H_2O_2 + Br^- \xrightarrow{1.4 \times 10^{-2}\ M^{-2}\ s^{-1}} H_2O + HOBr \qquad (23)$$

Updated: 4 September 2013

Print version

CEE 697K
ENVIRONMENTAL REACTION KINETICS

Lecture #2b

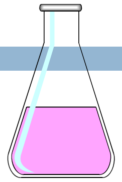
Introduction: Simple Rate Laws

Brezonik, pp.31-39

David A. Reckhow

Introduction

Variable Kinetic Order



- Any reaction order, except n=1

$$\boxed{\frac{dc}{dt} = -k_n c^n}$$

$$\boxed{\frac{1}{c^{n-1}} = \frac{1}{c_o^{n-1}} + (n-1)k_n t}$$

$$\boxed{c = c_o \frac{1}{\left[1+(n-1)k_n c_o^{n-1} t\right]^{1/(n-1)}}}$$

Half-lives

- Time required for initial concentration to drop to half, i.e.., $c=0.5c_o$
  - For a zero order reaction:

$$c = c_o - kt$$

$$0.5c_o = c_o - kt_{1/2}$$

$$t_{1/2} = \frac{0.5c_o}{k}$$

  - For a first order reaction:

$$c = c_o e^{-kt}$$

$$0.5c_o = c_o e^{-kt_{1/2}}$$

$$t_{1/2} = \frac{\ln(2)}{k} = \frac{0.693}{k}$$

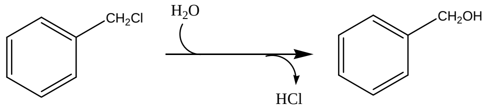
Example: Benzyl Chloride

- Use:
  - Manufacture of benzyl compounds, perfumes, pharmaceuticals, dyes, resins, floor tiles
- Toxicity
  - Intensely irritating to skin, eyes, large doses can cause CNS depression
- Emission
  - 45,000 lb/yr
- Fate
  - Benzyl chloride undergoes slow degradation in water to benzyl alcohol

Benzyl chloride II

Sources:
•Schwarzenbach et al., 1993, Env. Organic Chemistry
•1972, J. Chem.Soc. Chem. Comm. 425-6
•1967, Acta Chem. Scand. 21:397-407
•1961, J. Chem. Soc. 1596-1604

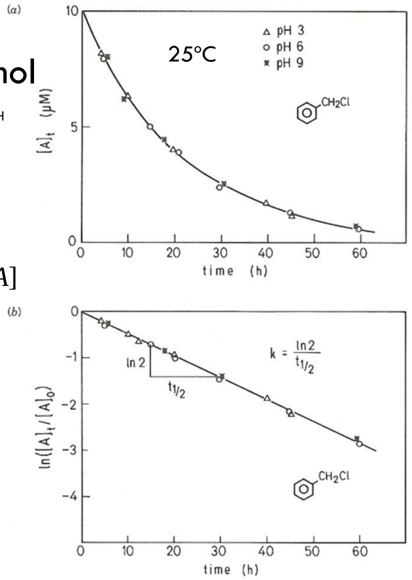
- ☐ Benzyl chloride to benzyl alcohol



  - Nucleophilic substitution
    - S_N1 or S_N2?
      - How to distinguish?
        - Salt effects

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

	Temperature	
	0.1°C	25°C
K	$0.042 \times 10^{-5}\ s^{-1}$	$1.38 \times 10^{-5} s^{-1}$
$T_{1/2}$	19.1 d	0.58 d



Mixed Second Order

$$A + B \xrightarrow{k_2} products$$

- ☐ Two different reactants

$$rate \equiv \frac{1}{V}\frac{d\xi}{dt} \equiv \frac{1}{\nu_A}\frac{d[A]}{dt} =$$

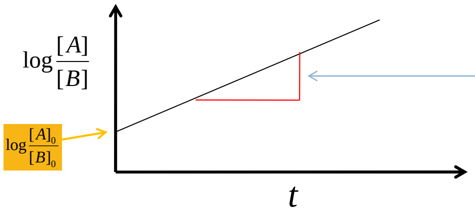
$$\boxed{\begin{aligned}\frac{dx}{dt} &= k_2[A][B] \\ &= k_2([A]_0 - x)([B]_0 - x)\end{aligned}}$$

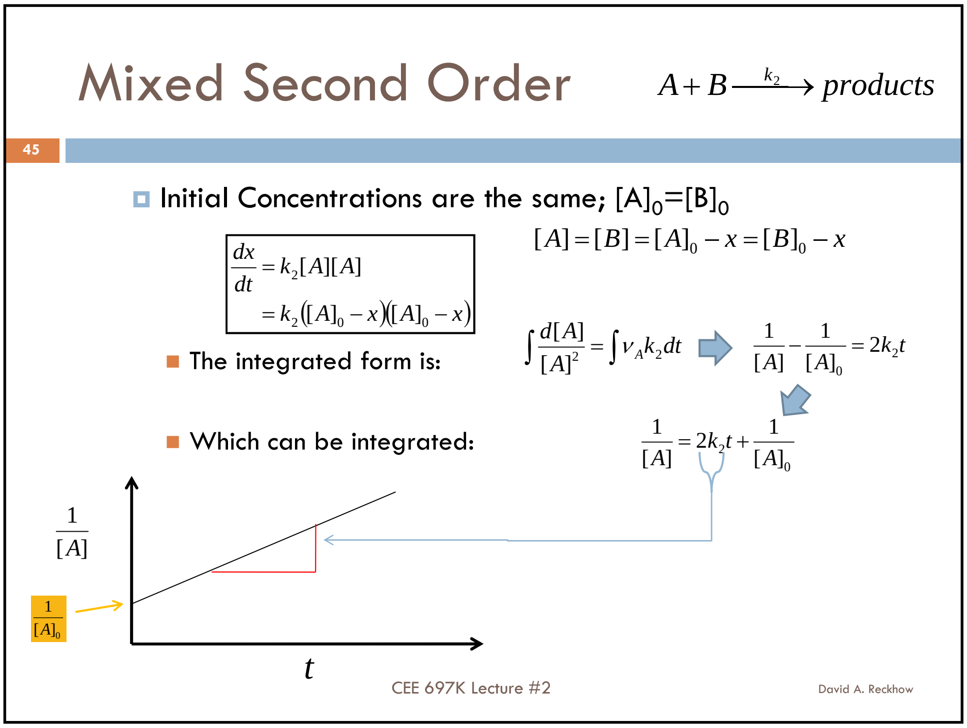
  - Initial Concentrations are different; $[A]_0 \neq [B]_0$
    - The integrated form is:

$$\frac{1}{[A]_0 - [B]_0}\ln\frac{[B]_0[A]}{[A]_0[B]} = k_2 t$$

    - Which can be expressed as:

$$\log\frac{[A]}{[B]} = \underbrace{0.43k_2([A]_0 - [B]_0)}t - \log\frac{[B]_0}{[A]_0}$$





Mixed Second Order

$A + B \xrightarrow{k_2} products$

- Initial Concentrations are the same; $[A]_0=[B]_0$

$$[A]=[B]=[A]_0-x=[B]_0-x$$

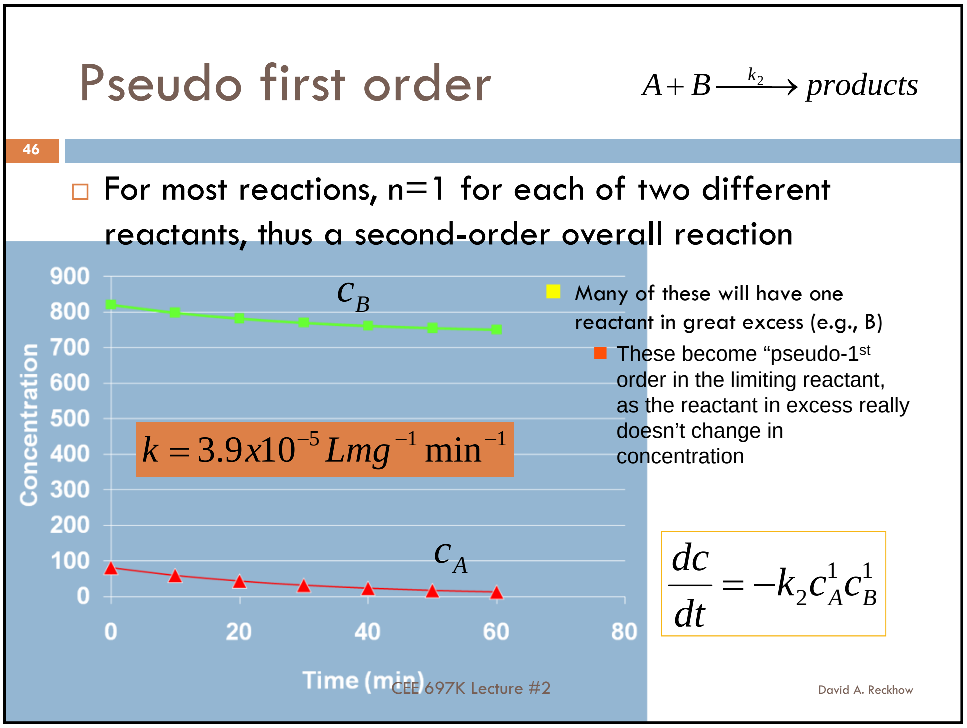
$$\boxed{\begin{aligned}\frac{dx}{dt} &= k_2[A][A]\\ &= k_2([A]_0-x)([A]_0-x)\end{aligned}}$$

- The integrated form is:

$$\int\frac{d[A]}{[A]^2}=\int \nu_A k_2 dt \Rightarrow \frac{1}{[A]}-\frac{1}{[A]_0}=2k_2t$$

- Which can be integrated:

$$\frac{1}{[A]}=\underbrace{2k_2}t+\frac{1}{[A]_0}$$



Pseudo first order

$A + B \xrightarrow{k_2} products$

- For most reactions, n=1 for each of two different reactants, thus a second-order overall reaction

$$k = 3.9x10^{-5}\,Lmg^{-1}\,\min^{-1}$$

- Many of these will have one reactant in great excess (e.g., B)
  - These become "pseudo-1st order in the limiting reactant, as the reactant in excess really doesn't change in concentration

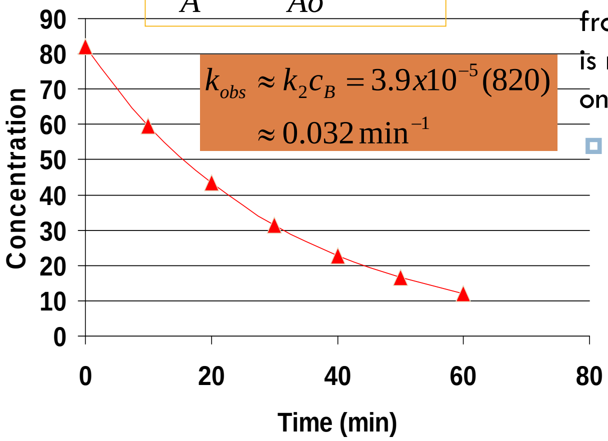
$$\boxed{\frac{dc}{dt}=-k_2c_A^1c_B^1}$$

Pseudo-1st order (cont.)

$$\frac{dc}{dt} = -k_2 c_A^1 c_B^1$$

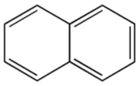
$$c_A = c_{Ao} e^{-k_{obs} t}$$

$$k_{obs} \approx k_2 c_B = 3.9x10^{-5}(820)$$
$$\approx 0.032 \min^{-1}$$



- Since C_2 changes little from its initial 820 mg/L, it is more interesting to focus on C_A
  - C_A exhibits simple 1st order decay, called pseudo-1st order
    - The pseudo-1st order rate constant is just the "observed rate" or k_{obs}

Example: O_3 & Naphthalene



- How long will it take for ozone (4.8 mg/L dose) to reduce the concentration of naphthalene by 99%?
  - Used in moth balls and as a chemical intermediate
  - 2nd order reaction; k_2 = 3000 $M^{-1}s^{-1}$
    - Table 1 in Hoigne & Bader, 1983 [Wat. Res. 17:2:173]
- Industrial WW with 0.1mM naphthalene
  - Both reactants are at same (0.1mM) concentration
    - Therefore, this reduces to a simple 2nd order reaction

$$\frac{1}{[A]} = \frac{1}{[A]_0} + k_2 t$$

$$\frac{1}{10^{-6}} = \frac{1}{10^{-4}} + 3000t$$

$$3000t = 990{,}000$$
$$t = 330\,\text{sec}$$
$$= 5.5\,\text{min}$$

O_3 & Naphthalene (cont.)

- Contaminated river water (0.001 mM)
  - Now ozone is in great molar excess, so this is a pseudo-1st order reaction $[A]=[A]_0 e^{-k_2[B]_0 t}$

$$\ln\left({}^{[A]}\!\big/_{[A]_0}\right) = -k_2[B]_0 t$$

$$\ln\left({}^{10^{-8}}\!\big/_{10^{-6}}\right) = -3000\left(10^{-4}\right)t$$

$$-4.605 = -0.3t$$

$$t = 15.4\,\text{sec}$$

Molecularity of three: 3rd order kinetics

- Quite improbably, but sometimes happens
  - Three different reactants $A+B+C \xrightarrow{k_3} products$

$$\frac{dx}{dt} = k_3[A][B][C] = k_3\left([A]_0 - x\right)\left([B]_0 - x\right)\left([C]_0 - x\right)$$

    - Complicated integrated form exists
  - Two different reactants $2A+B \xrightarrow{k_3} products$

$$\frac{dx}{dt} = k_3[A]^2[B] = k_3\left([A]_0 - 2x\right)^2\left([B]_0 - x\right)$$

    - Integrated form:

$$\frac{\left([A]_0 - [A]\right)\left(2[B]_0 - [A]_0\right)}{[A]_0[A]} + \ln\frac{[B]_0[A]}{[A]_0[B]} = \left(2[B]_0 - [A]_0\right)^2 k_3 t$$

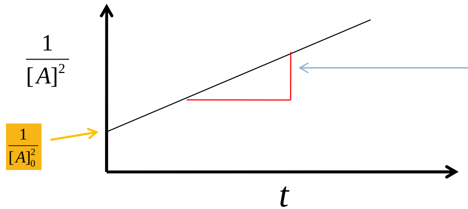
3rd Order (cont.)

$$3A \xrightarrow{k_3} products$$

- Only one reactant or Initial Concentrations are the same

$$\boxed{\begin{aligned}\frac{dx}{dt} &= k_3[A][A][A] \\ &= k_3([A]_0 - x)([A]_0 - x)([A]_0 - x)\end{aligned}}$$

  - The integrated form is: $\int \frac{d[A]}{[A]^3} = \int \nu_A k_3 dt \Rightarrow \frac{1}{[A]^2} - \frac{1}{[A]_0^2} = -2\nu_A k_3 t = 6k_3 t$
  - Which can be integrated: $\frac{1}{[A]^2} = \underbrace{6k_3}_{} t + \frac{1}{[A]_0^2}$



3rd Order (cont.)

- Pseudo-2nd order reactions
  - When one of the reactants has a fixed concentration
    - E.g., present in excess or buffered, or acts catalytically
  - Like a regular 2nd order reaction with two reactants but observed constant is fundamental rate constant times concentration of the 3rd reactant.
- The integrated form:

$$\frac{1}{[A]_0 - [B]_0} \ln \frac{[B]_0[A]}{[A]_0[B]} = \underbrace{k_3[C]}_{k_{obs}} t$$

Example: chlorate formation

- Formation of chlorate in concentrated hypochlorite solutions
  - Concern: chlorate is toxic
    - MCLG=0.2 mg/L
  - Stoichiometry

$$3OCl^- \rightarrow ClO_3^- + 2Cl^-$$

    - Is this 3rd order? Be skeptical!
  - Observed kinetics

$$\frac{d[ClO_3^-]}{dt} = k_{obs}\left[OCl^-\right]^2$$

    - So, why is it 2nd order?

Chlorate example (cont.)

- Answer: this is a reaction pathway composed of two elementary reactions
  - Step #1 $2OCl^- \xrightarrow{slow} ClO_2^- + Cl^-$
  - Step #2 $OCl^- + ClO_2^- \xrightarrow{fast} ClO_3^- + Cl^-$
- In multi-step reactions such as these, we say that
  - the overall rate is determined by the slowest step
    - Called the "rate-limiting step" or RLS
  - Rate law is written based on the RLS
    - Subsequent steps are ignored
    - Prior steps are incorporated as they determine the concentrations of the RLS reactants

Homework #2 is based on this reaction

Reversible reaction kinetics

For a general reversible reaction:

$$aA + bB \underset{k_r}{\overset{k_f}{\leftrightarrow}} pP + qQ$$

And the rate law must consider both forward and reverse reactions:

$$rate = k_f C_A^a C_B^b - k_r C_P^p C_Q^q$$

where,

k_f = forward rate constant, [units depend on a and b]

k_b or k_r = backward rate constant, [units depend on a and b]

C_P = concentration of product species P, [moles/liter]

C_Q = concentration of product species Q, [moles/liter]

p = stoichiometric coefficient of species P

q = stoichiometric coefficient of species Q

Reversible 1st order reactions

- Kinetic law

$$\frac{dB}{dt} = k_1[A] - k_2[B]$$

- Eventually the reaction slows and,
  - Reactant concentrations approach the equilibrium values

$$\frac{dB}{dt} = 0 = k_1[A] - k_2[B]$$

$$\frac{[B]}{[A]} = \frac{k_1}{k_2} \equiv K_{eq}$$

Stumm & Morgan
Fig. 2.10
Pg. 69

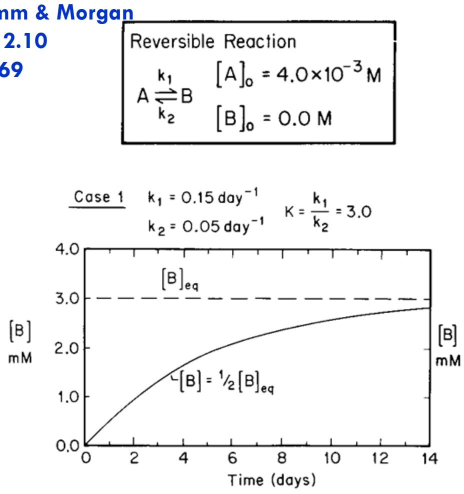


Figure 2.10. Single reversible reaction.

Reversible 1st order (cont.)

$$A \underset{k_r}{\overset{k_f}{\leftrightarrow}} P$$

- Solution to non-equilibrium reaction period
  - See Brezonik, pg 37-38 for details

$$[A] = \frac{1}{k^*}[A]_0 \left\{ k_r + k_f e^{-k^* t} \right\}$$

    - Where $k^* = k_f + k_r$
  - And: $$\frac{[A]-[A]_{equ}}{[A]-[A]_{equ}} = e^{-k^* t}$$ Linearized version
  - Where: $$\frac{k_f}{k_r}\left(= K_{equ}\right) = \frac{[P]_{equ}}{[A]_{equ}}$$

- To next lecture