CBE 40445

9/7/20 "LABOR DAY"

SO FAR WE HAVE EXAMINED THE BASIC ASPECTS OF CHEMICAL REACTORS + REACTION KINETICS

BATCH

$$V\frac{dC_i}{dt} = \nu_i r V$$

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

PFR

$$\frac{dF_i}{dV} = \nu_i r$$

$$\tau = \frac{V}{q}$$

$$\frac{dC_A}{d\tau} = -kC_A$$

CSTR

$$0 = F_{A0} - F_A - r_A V$$

$$= q C_{A0} - q C_A - k C_A V$$

$$\frac{C_A}{C_{A0}} = \frac{1}{1 + k\tau}$$

KINETICS

$$A \rightarrow M \qquad r = k C_A$$

$$A + B \rightarrow 2M \qquad r = k C_A C_B$$

$$A + E \underset{k_r}{\overset{k_1}{\rightleftharpoons}} AE \xrightarrow{k_2} M + E$$

$$r = -\frac{k_1 k_2 C_A C_E^0}{k_1 C_A + k_2 + k_r}$$

COULD BE 0 ORDER: $k_1 C_A >> k_2 + k_r$

OR 1ST ORDER $k_1 C_A << k_2 + k_r$

FOR SIMPLE CASES, A LINEAR PLOT COULD PROVIDE A REASONABLE VALUE FOR k,

OTHERWISE... NONLINEAR FITTING.

(NOT TO FORGET) THERMODYNAMICS

$$\Delta G^\circ = -RT \ln K_a$$

$$K_a = \left(\frac{X_M^m \; X_N^n}{X_A^a \; X_B^b}\right)\left(\frac{\phi_M^m \; \phi_N^n}{\phi_A^a \; \phi_B^b}\right)\left(\frac{P}{P_0}\right)^{m+n-a-b}$$

A "COMPLICATION" THAT HAS NOT YET BEEN ADDRESSED

$$\bar{a}A + \bar{b}B \ldots \longrightarrow \bar{s}S + \bar{w}W + \ldots$$

SUPPOSE # MOLES IS NOT SAME FOR BOTH REACTANTS + PRODUCTS...

DEFINE "ε" (IN TERMS OF LIMITING REACTANT, SAY 'A')

$$n_{TOTAL} = n^{o}_{TOTAL}\left(1 + \varepsilon_A f_A\right)$$

$$\varepsilon_A = \frac{\text{MOLES PRODUCTS}}{\text{MOLES OF REACTANTS}}$$

$$= \frac{n_A^{o}}{n^{o}_{TOTAL}} \frac{\sum_i \nu_i}{|\nu_A|}$$

ONLY AN ISSUE FOR
GAS PHASE

Ex:

$$\overset{1}{C_6H_{14}} \rightarrow \overset{1}{C_6H_6} + \overset{4}{4\,H_2}$$

$$\varepsilon_A = \frac{4+1-1}{|-1|} = 4$$

BATCH → CONST P → V INCREASES

$$P = P^0(1+\varepsilon_A f_A)$$

CONST V → P INCREASES

$$V = V^0(1+\varepsilon_A f_A)$$

FLOWING SYSTEM → q INCREASES

$$q = q^0(1+\varepsilon_A f_A)$$

1 OTHER HOUSEKEEPING ITEM

DON'T ALWAYS BELIEVE WHAT YOU READ.

Contents lists available at ScienceDirect
Bioresource Technology
journal homepage: www.elsevier.com/locate/biortech

Cell growth kinetics of *Chlorella sorokiniana* and nutritional values of its biomass

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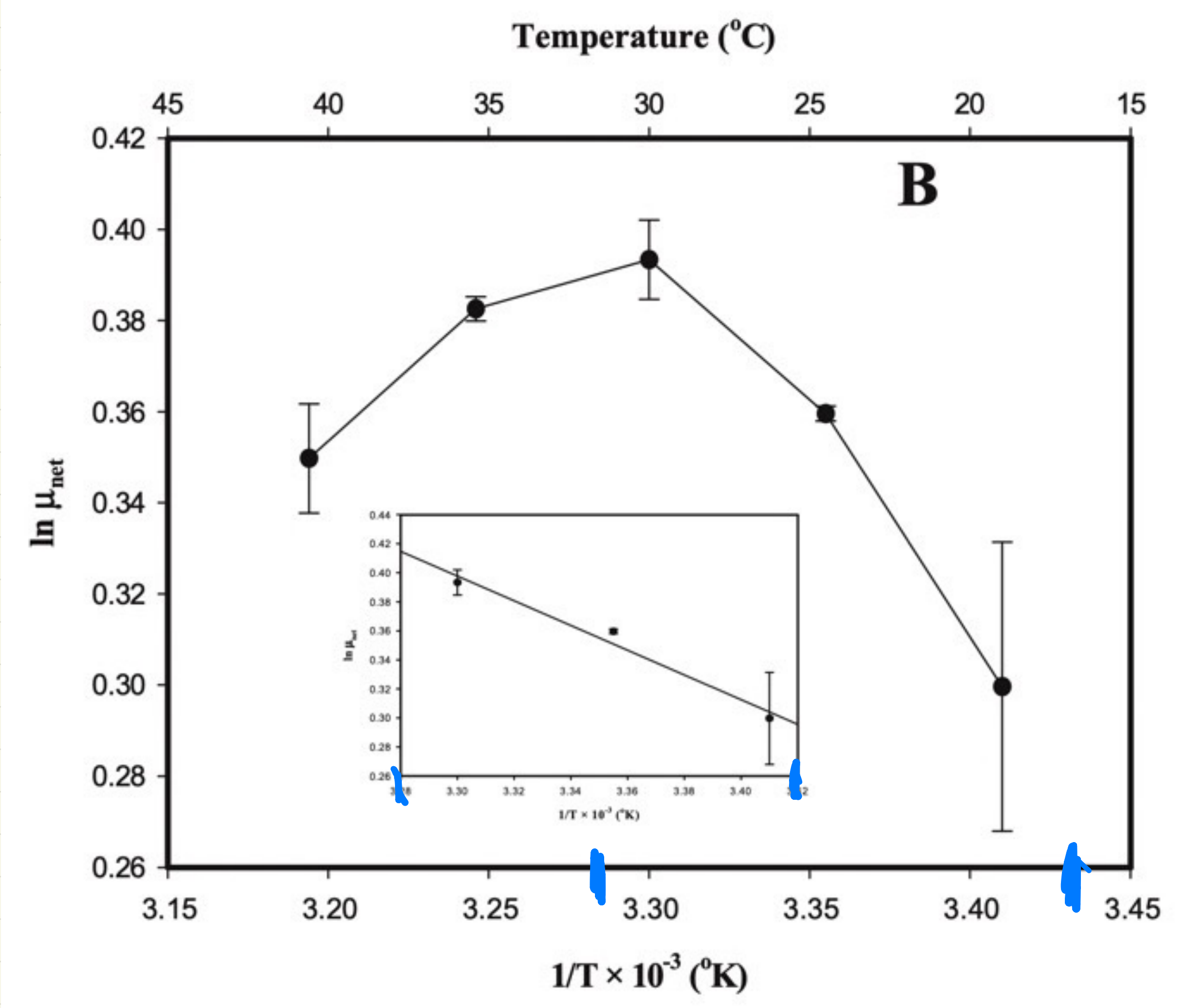

!!

Thermostable α-amylase and α-galactosidase production from the thermophilic and aerobic *Bacillus* sp.JF strain

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strate is expressed by the Lineweaver–Burk relationship as shown in Fig. 3. The experiment data produce a single straight line (Fig. 3), and so the cell growth can be described by the model of Monod [8,11]. When the constants were calculated using the experiment data, the μ_{max} was 0.084 (1/h), the K_s was 22.1 (g/l), i.e. the specific growth rate μ is

$$\mu = \frac{\mu_{max} S}{K_s + S} = \frac{0.084 S}{22.1 + S} \qquad (1)$$

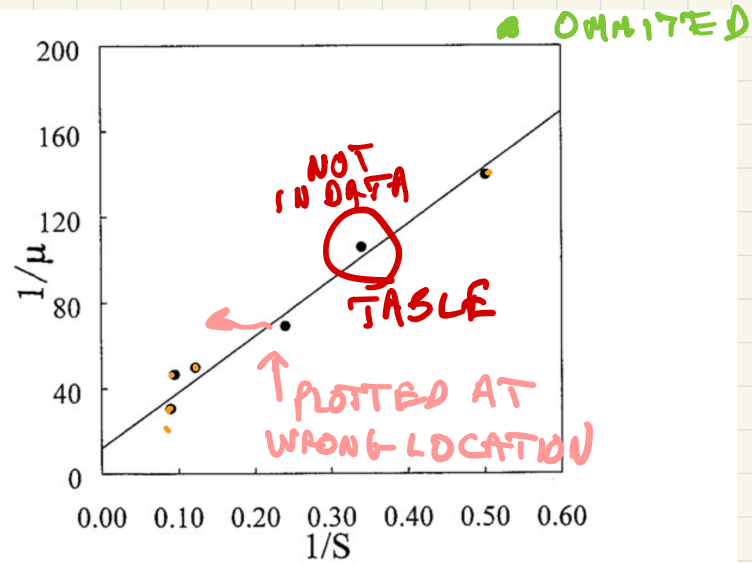


Fig. 3. Lineweaver–Burk on cell growth to substrate. ●, experiment point. Batch culture at 60°C in 30 l fermentor.

Fermentation time (h)	Total sugar (g/l)	Reducing sugar (g/l)	Cells (g/l)
0	11.8	2.01	0.155
2	11.6	1.99	0.162
4	10.9	1.18	0.168
6	9.74	1.87	0.192
10	9.16	1.76	0.216
16	5.80	1.40	0.236
22	2.12	1.27	0.256
28	1.92	0.43	0.258
31	1.74	0.36	0.260
36	1.73	0.32	0.262
47	1.40	0.26	0.267
52	1.36	0.24	0.268

CHAPTER 4

(MORE DETAILED) EXAMINATION OF MULTI-STEP (CATALYTIC) REACTIONS

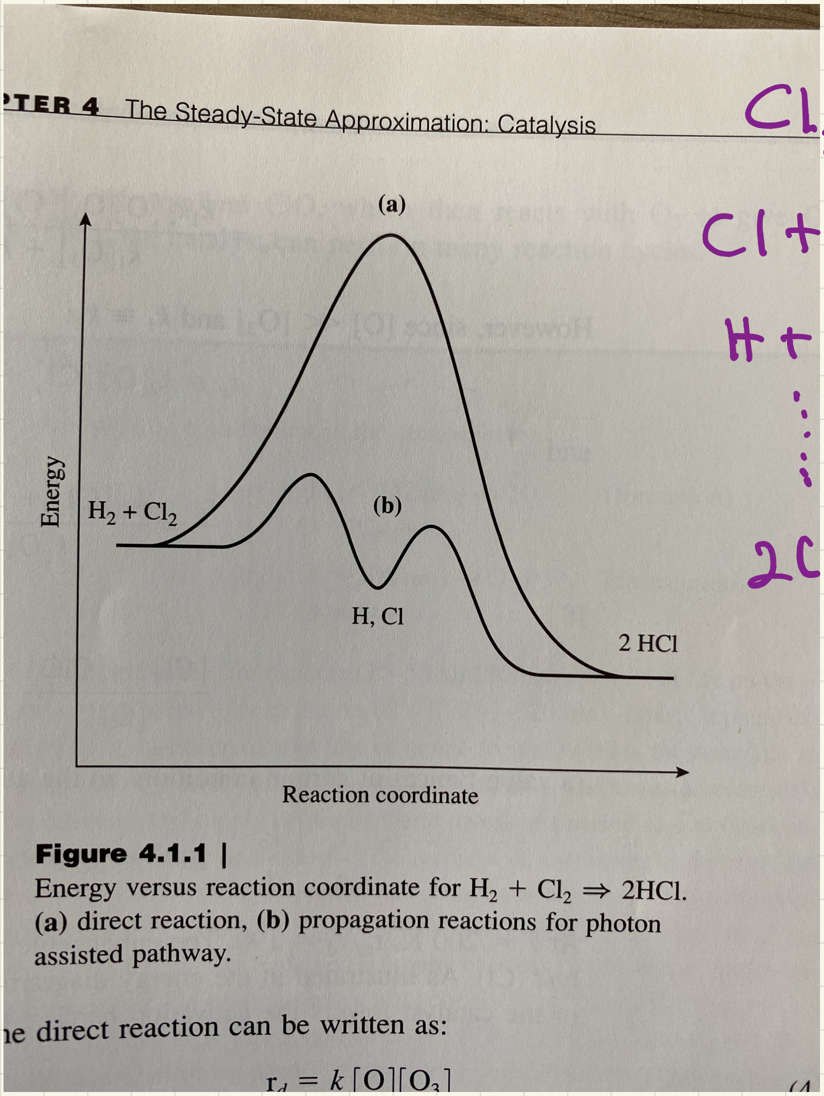


Figure 4.1.1 |
Energy versus reaction coordinate for $H_2 + Cl_2 \Rightarrow 2HCl$. (a) direct reaction, (b) propagation reactions for photon assisted pathway.

ne direct reaction can be written as:

$r_d = k[O][O_3]$

$Cl_2 \xrightarrow{h\nu} 2Cl$ INITIATION

$Cl + H_2 \rightarrow HCl + H$ PROPAGATION

$H + Cl_2 \rightarrow HCl + Cl$ PROPAGATION

⋮

$2Cl \rightarrow Cl_2$ TERMINATION

OZONE DECOMPOSITION

At T = 200 K, r_c/r_d = 190. ... Figure 4.1.2, ...
lyst (Cl). As illustrated in the energy diagram shown in Figure 4.1.2, ...
of the catalyst lowers the activation barrier. The Cl catalyst first reacts with O to

$O + O_3 \rightarrow 2O_2$

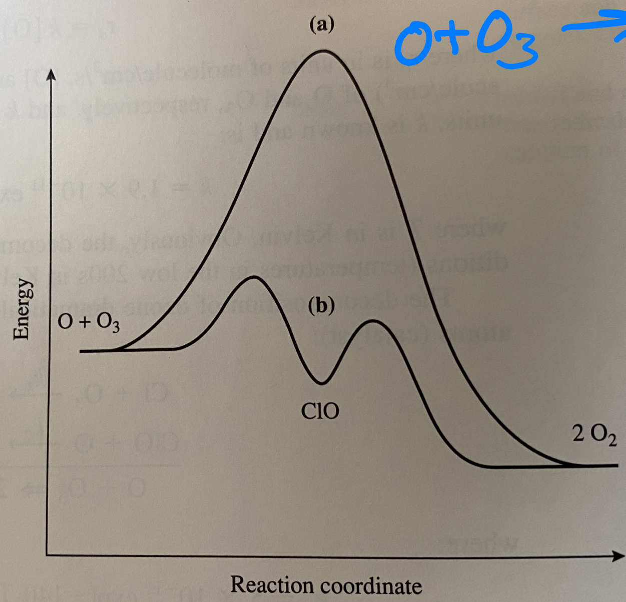


Figure 4.1.2 | Energy versus reaction coordinate for ozone decomposition. (**a**) direct reaction, (**b**) Cl catalyzed reaction.

$r = k[O][O_3]$

$k = 1.9 \times 10^{-11} \exp\left(-\frac{2300}{T}\right)$

"SLOW" !!

IF CHLORINE IS PRESENT...

$$Cl + O_3 \xrightarrow{k_1} O_2 + ClO$$

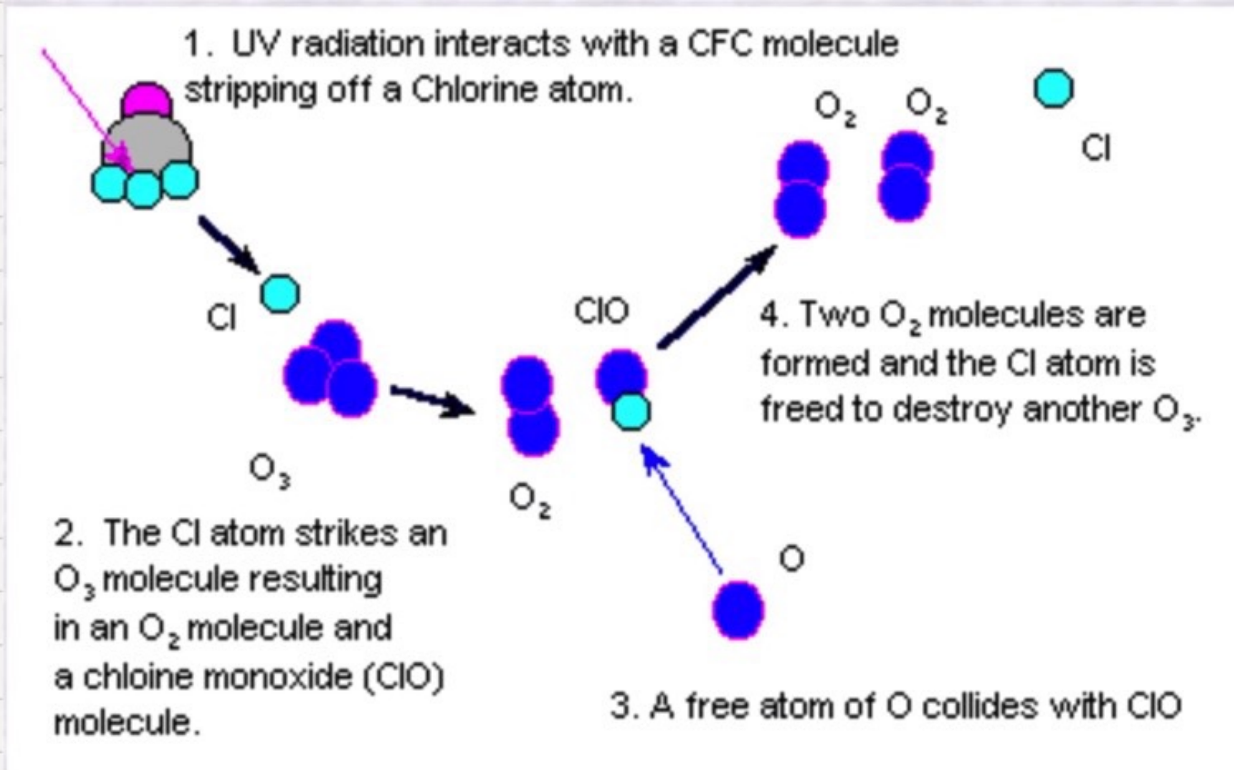
$$ClO + O \xrightarrow{k_2} O_2 + Cl$$

$$O + O_3 \rightarrow 2O_2$$

$$k_1 = 5 \times 10^{-11} \exp\left(-\frac{140}{T}\right)$$

$$k_2 = 1.1 \times 10^{-10} \exp\left(-\frac{220}{T}\right)$$

$\frac{cm^3}{s \text{ MOLECULE}}$



. Paul Crutzen, Mario J. Molina and F. Sherwood Rowland won the Nobel prize in chemistry

CAN SHOW . . .

$$r_c = \frac{k_1 k_2 [O][O_3]([Cl]+[ClO])}{k_1[O_3] + k_2[O]}$$

BUT $[O] \ll [O_3]$ $\quad k_1 \cong k_2$

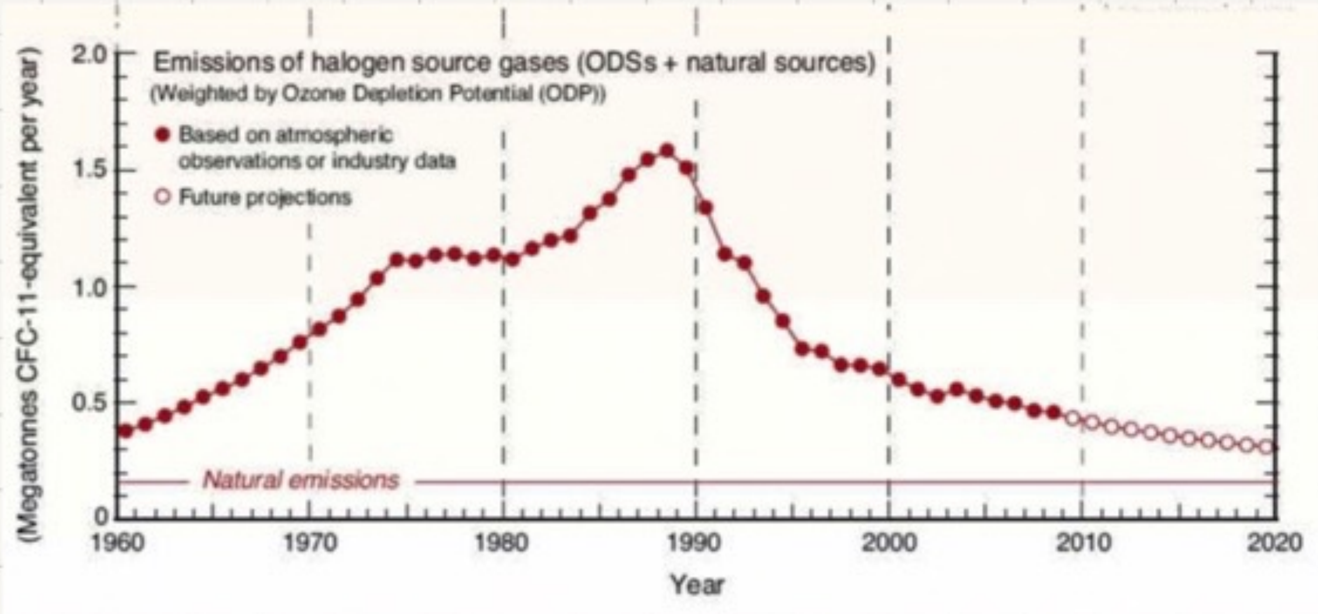
$$r_c = k_2([O][Cl]+[ClO])$$

$$\frac{\text{CATALYZED } r_c}{\text{DIRECT } r_d} = k_2 \frac{([Cl]+[ClO])}{k_3[O_3]}$$

ALSO $\quad \frac{[Cl]+[ClO]}{[O_3]} \sim 10^{-3}$

$$\frac{r_c}{r_d} = \frac{k_2}{k} \times 10^{-3} = 6 \times 10^{-3} \exp\left(\frac{2050}{T}\right)$$

@ T = 200 K, $\quad \frac{r_c}{r_d} = 200$

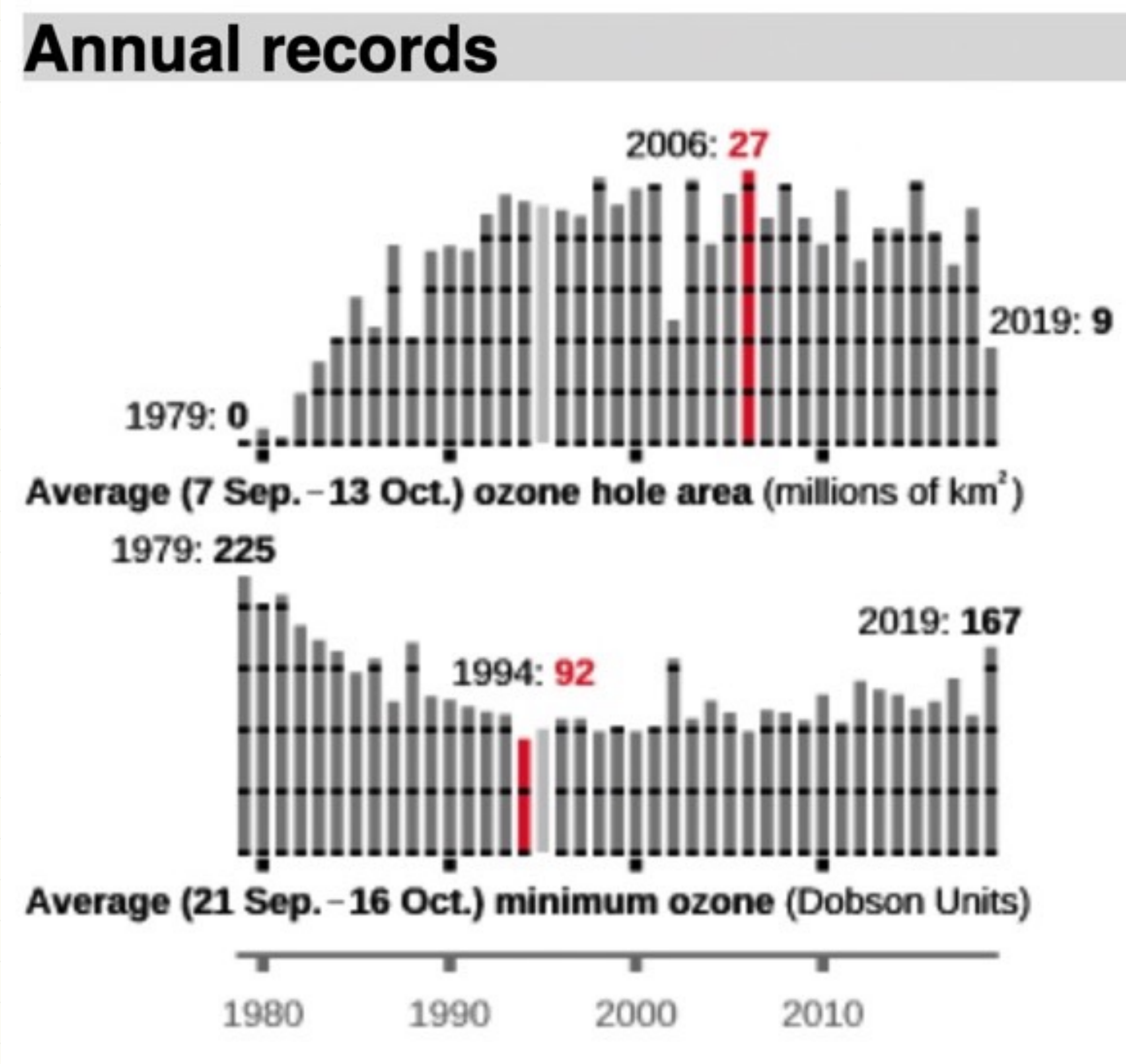


Emissions of halogen source gases (ODSs + natural sources)
(Weighted by Ozone Depletion Potential (ODP))
Based on atmospheric observations or industry data
Future projections
Natural emissions
(Megatonnes CFC-11-equivalent per year)
2.0
1.5
1.0
0.5
0
1960
1970
1980
1990
2000
2010
2020
Year

2019 Ozone Hole is the Smallest on Record Since Its Discovery

Abnormal weather patterns in the upper atmosphere over Antarctica dramatically limited ozone depletion in September and October, resulting in the smallest ozone hole observed since 1982, NASA and NOAA scientists reported today.

"It's great news for ozone in the Southern Hemisphere," said Paul Newman, chief scientist for Earth Sciences at NASA's Goddard Space Flight Center in Greenbelt, Maryland. "But it's important to recognize that what we're seeing this year is due to warmer stratospheric temperatures. It's not a sign that atmospheric ozone is suddenly on a fast track to recovery."



FINALLY ... THE REAL NAME OF THE CHAPTER ...

THE STEADY-STATE APPROXIMATION

CONSIDER

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$C_A(t=0) = C_{A0}$, $C_{B0} = 0$, $C_C^0 = 0$

$$x \equiv \frac{C_A}{C_A^0} \qquad y = \frac{C_B}{C_A^0} \qquad w = \frac{C_C}{C_A^0}$$

$$\frac{dx}{dt} = -k_1 x$$

$$\frac{dy}{dt} = k_1 x - k_2 y$$

$$\frac{dw}{dt} = k_2 y$$

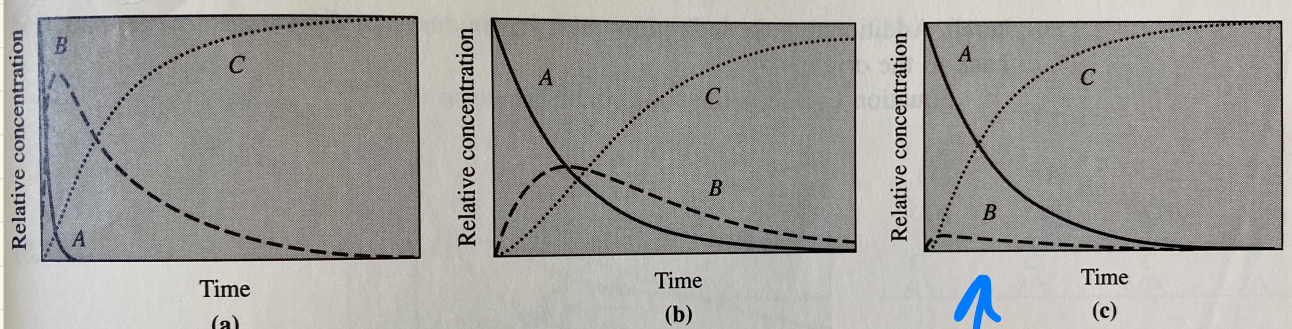
^0_A denotes the concentration of A ...
nce equations for this system are:

$$\frac{dx}{dt} = -k_1 x \qquad \frac{dy}{dt} = k_1 x - k_2 y \qquad \frac{dw}{dt} = k_2 y \tag{4.2.1}$$

ere $x = C_A/C_A^0$, $y = C_B/C_A^0$, and $w = C_C/C_A^0$. Integration of Equation (4.2.1)
h $x = 1$, $y = 0$, $w = 0$ at $t = 0$ gives:

$$\left.\begin{aligned} x &= \exp(-k_1 t) \\ y &= \frac{k_1}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] \\ w &= 1 - \frac{k_2}{k_2 - k_1}\exp(-k_1 t) + \frac{k_1}{k_2 - k_1}\exp(-k_2 t) \end{aligned}\right\} \tag{4.2.2}$$

BEING GOOD CHEMICAL ENGINEERS WE PLOT THE RESULT



THIS LOOKS INTERESTING

Figure 4.2.1 |
Two first-order reactions in series.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

(a) $k_2 = 0.1\, k_1$, (b) $k_2 = k_1$, (c) $k_2 = 10\, k_1$.

NOT MUCH B, AND DOESN'T CHANGE..

$(k_2 \gg k_1)$

$$x = \exp(-k_1 t)$$

$$y = \frac{k_1}{k_2} \exp(-k_1 t)$$

$$w = 1 - \exp(-k_1 t)$$

THIS IS THE SOLUTION TO!

$$\frac{dx}{dt} = -k_1 x$$

$$0 = k_1 x - k_2 y$$

$$\frac{dw}{dt} = k_2 y$$

THUS WE PRESUME!

$$\frac{dy}{dt} = 0$$

"STEADY-STATE" ASSUMPTION.

WE WILL USE ("TRYOUT") THIS SIMPLIFICATION FOR REACTION INTERMEDIATES ...