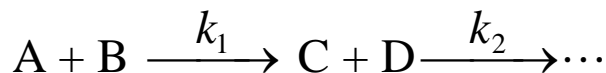


# T Dependence of Complex Reactions

Assume some complex reaction



for which the overall reaction rate constant can be expressed in terms of the elementary steps:

$$k_{\text{overall}} = \frac{k_1^{n_1} k_2^{n_2} \dots}{k_3^{n_3} \dots}$$

If each rate constant obeys the Arrhenius expression,

$$k_i = A_i e^{-E_i/RT}$$

$$k_{\text{overall}} = \left( \frac{A_1^{n_1} A_2^{n_2} \dots}{A_3^{n_3} \dots} \right) \exp \left\{ - (n_1 E_1 + n_2 E_2 - n_3 E_3 - \dots) / RT \right\}$$

i.e. The Arrhenius parameters are

$$A_{\text{overall}} = \prod_i A_i^{n_i}$$

$$E = \sum_i n_i E_i$$

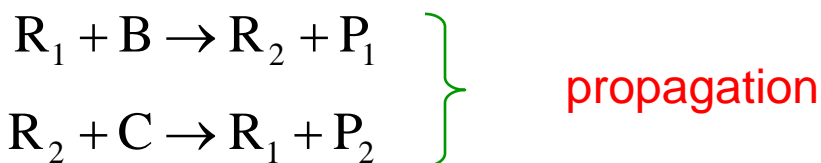
The overall “activation energy” may be negative, if  $n_i$  is negative and the corresponding  $E_i$  is large enough.

Also, for a pre-equilibrium reaction where  $k_{\text{overall}} = K_1 k_2$

$$E_a = RT^2 \frac{d \ln k_{\text{overall}}}{dT} = RT^2 \frac{d \ln K_1}{dT} + E_2 = \Delta H_1 + E_2$$

$E_2$  is positive but  $\Delta H$  can be negative.

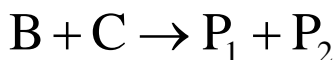
# Chain Reactions



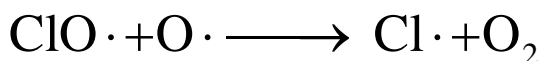
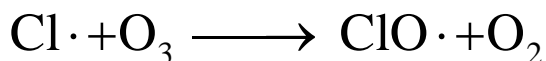
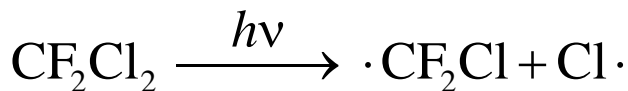
R is often, but not always, a free radical.

Initiation may be thermal, photochemical, radiolysis, ...

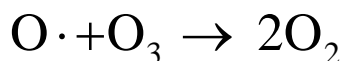
The overall reaction is determined by adding the propagation steps:



Important examples include polymerization, combustion, photochemical smog production and the depletion of stratospheric ozone by CFCs.

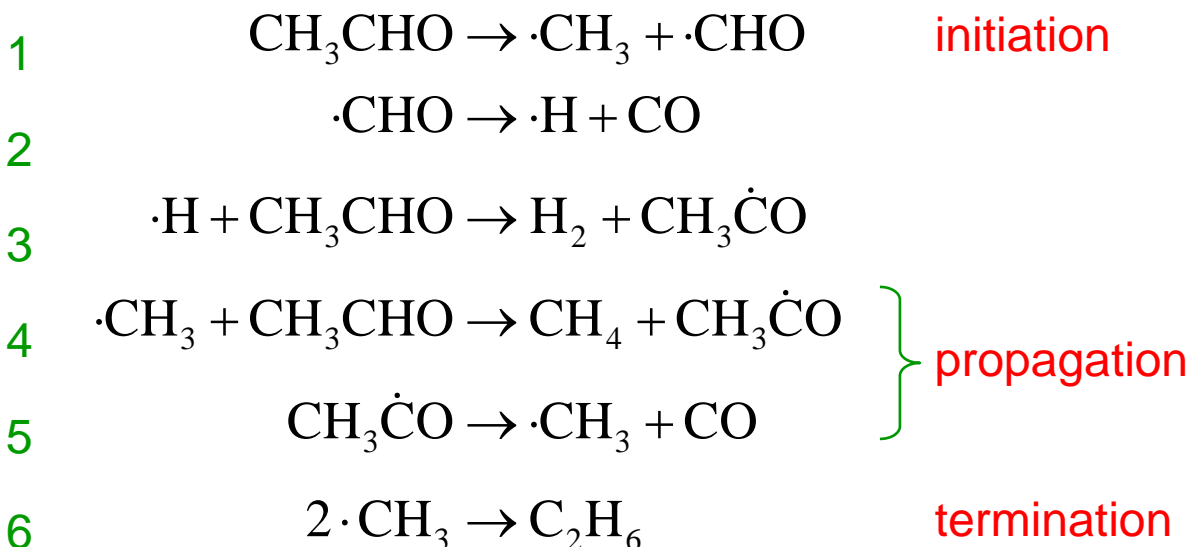


The net effect is catalysis by the CFC of the reaction



# Rice-Herzfeld Mechanism

e.g. for the thermal decomposition of acetaldehyde



Write steady-state equations for  $[\text{CHO}]$ ,  $[\text{H}]$ ,  $[\text{CH}_3]$ ,  $[\text{CH}_3\text{CO}]$ :

$$\frac{d}{dt}[\text{CHO}] = k_1[\text{CH}_3\text{CHO}] - k_2[\text{CHO}] = 0 \quad [\text{CHO}] = (k_1/k_2)[\text{CH}_3\text{CHO}]$$

$$\frac{d}{dt}[\text{H}] = k_2[\text{CHO}] - k_3[\text{H}][\text{CH}_3\text{CHO}] = 0 \quad [\text{H}] = (k_1/k_3)$$

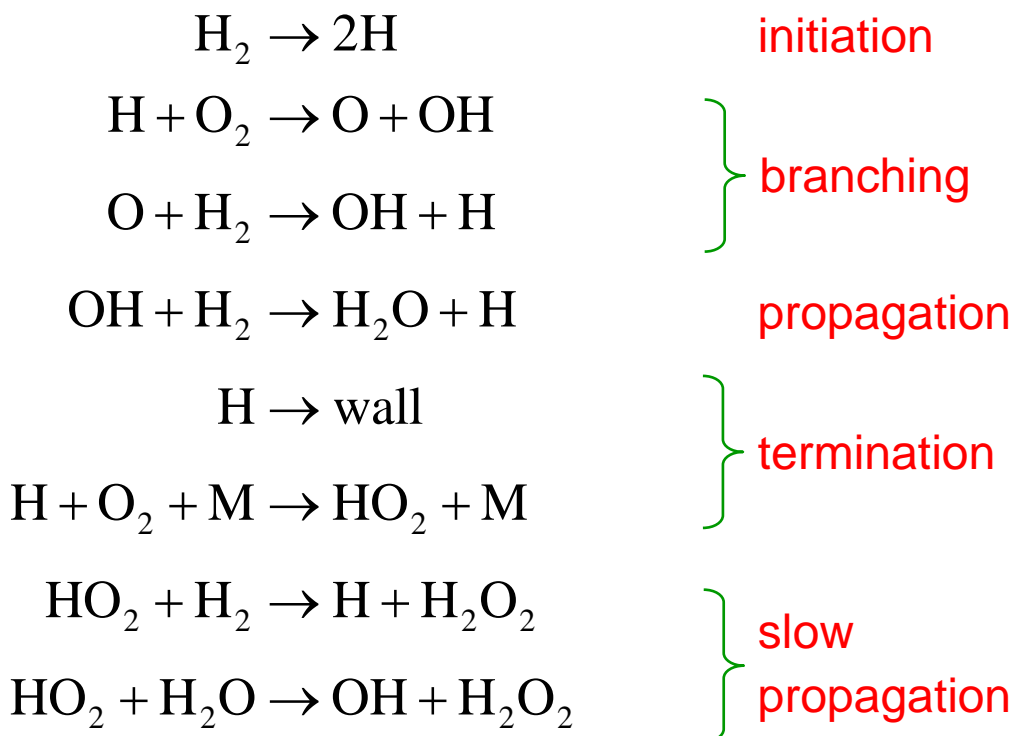
$$\frac{d}{dt}[\text{CH}_3\text{CO}] = k_4[\text{CH}_3][\text{CH}_3\text{CHO}] + k_3[\text{H}][\text{CH}_3\text{CHO}] - k_5[\text{CH}_3\text{CO}] = 0$$

$$\frac{d}{dt}[\text{CH}_3] = k_1[\text{CH}_3\text{CHO}] - k_4[\text{CH}_3][\text{CH}_3\text{CHO}] + k_5[\text{CH}_3\text{CO}] - 2k_6[\text{CH}_3]^2 = 0$$

$$[\text{CH}_3]^2 = (k_1/k_6)[\text{CH}_3\text{CHO}]$$

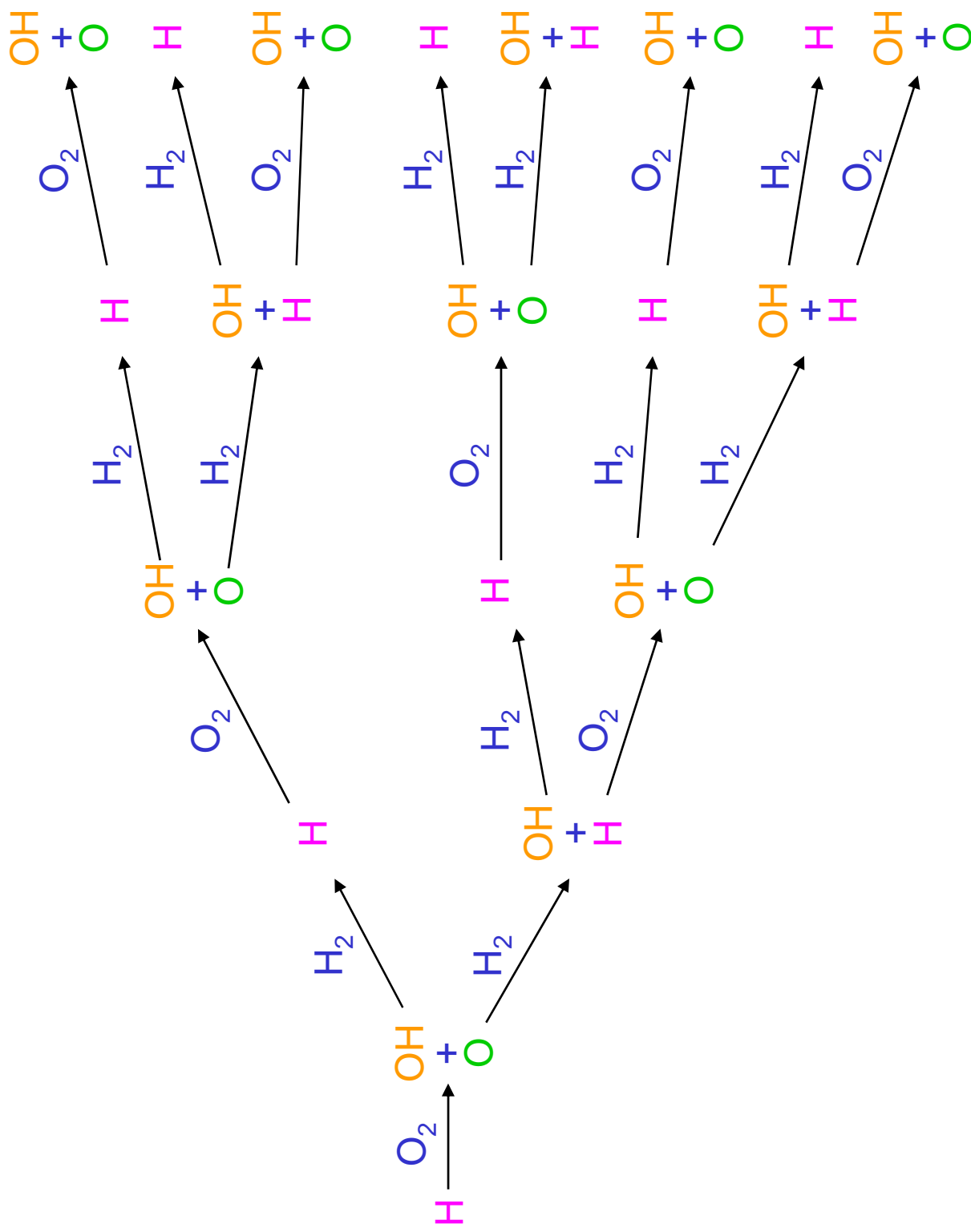
$$\text{rate} = \frac{d}{dt}[\text{CH}_4] = k_4[\text{CH}_3][\text{CH}_3\text{CHO}] = k_4(k_1/k_6)^{1/2}[\text{CH}_3\text{CHO}]^{3/2}$$

# An Explosive Reaction



At 700 K and 0.1 bar  $\text{O}_2$ ,

*each* initial H atom  $\rightarrow 10^{13}$  H atoms in 0.3 s.



# Branching Chain Reactions

- |   |                    |                                   |                 |
|---|--------------------|-----------------------------------|-----------------|
| 1 | Initiation         | $A, B \rightarrow R_1$            |                 |
| 2 | Branching          | $R_1 + A \rightarrow R_2 + R_3$   | [R] increases   |
| 3 | Propagation        | $B + R_i \rightarrow R_i + \dots$ |                 |
| 4 | Termination (wall) | $R_i \rightarrow P_1$             | } [R] decreases |
|   | (combination)      | $2R_i \rightarrow P_2$            |                 |

The steady-state approximation does not apply.

If  $n$  is the number of radicals at time  $t$ ,

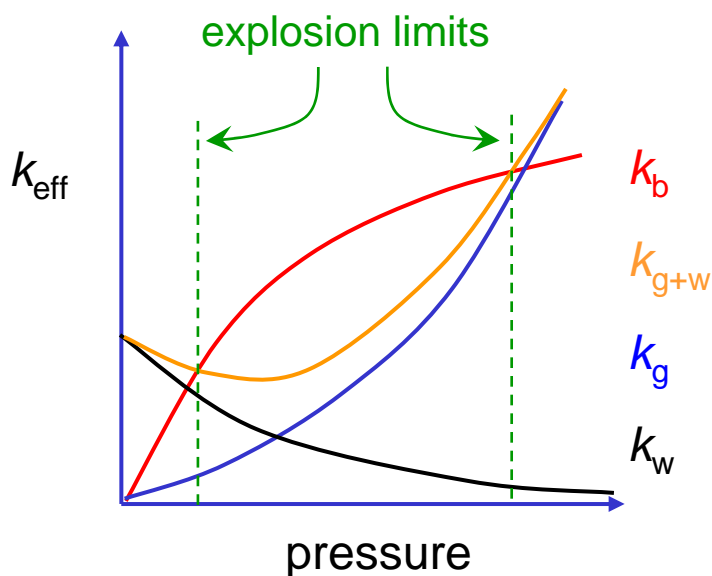
$$\frac{dn}{dt} = \rho_I + k_b n - (k_w + k_g) n$$

$$= \rho_I + \phi n$$

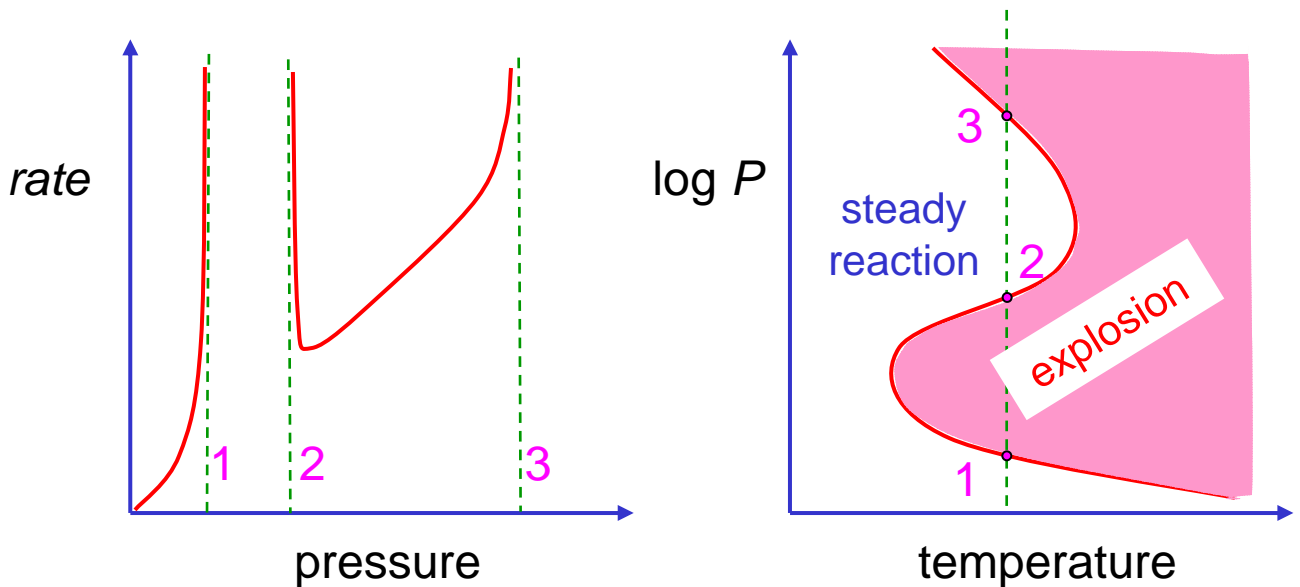
$$\phi = k_b - (k_w + k_g)$$

$$n = \frac{\rho_I}{\phi} (e^{\phi t} - 1)$$

The exponential increase in  $n$  for  $\phi > 0$  leads to explosion.



# Explosion Limits



At pressures below 1,

- wall termination is dominant
- the limit depends on surface composition and area
- the limit is altered by the size of the reaction vessel

Between 1 and 2,

- is the **explosion peninsula**
- the limits change with temperature because branching reactions are  $T$  dependent, diffusion less so

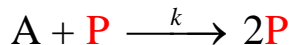
Between 2 and 3,

- gas phase termination reactions are dominant

At pressures above 3,

- reaction products are important
- heat from exothermic reactions → **thermal explosion**

# Autocatalysis



$$\text{rate} = -\frac{da}{dt} = \frac{dx}{dt} \quad [A] = a_0 - x, \quad [P] = p_0 + x$$

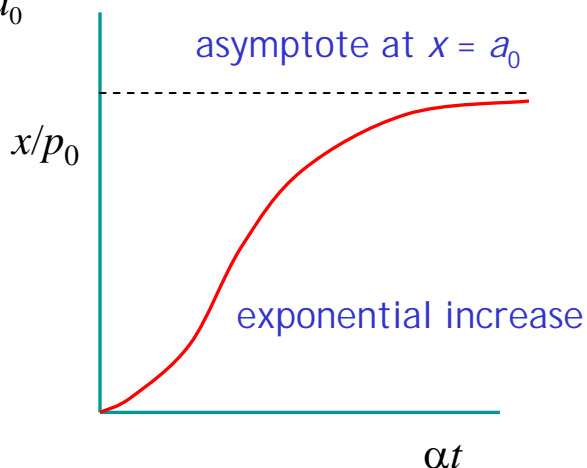
$$\frac{dx}{dt} = k(a_0 - x)(p_0 + x)$$

$$\begin{aligned} kt &= \int_0^x \left\{ \frac{dx}{(a_0 - x)(p_0 + x)} \right\} \\ &= \frac{1}{(a_0 + p_0)} \int_0^x \left\{ \frac{1}{(a_0 - x)} + \frac{1}{(p_0 + x)} \right\} dx \\ &= \frac{1}{(a_0 + p_0)} \left[ -\ln(a_0 - x) + \ln(p_0 + x) \right]_0^x \\ &= \frac{1}{(a_0 + p_0)} \ln \left\{ \frac{a_0}{(a_0 - x)} \frac{(p_0 + x)}{p_0} \right\} \end{aligned}$$

Substitute  $\alpha = (a_0 + p_0)k$ ,  $\beta = p_0/a_0$

$$\alpha t = \ln \frac{(1 + x/p_0)}{(1 - \beta x/p_0)}$$

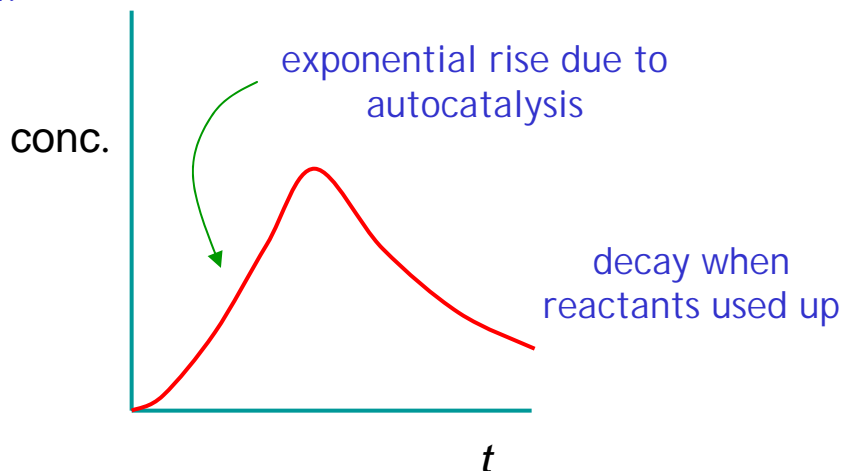
$$x/p_0 = \frac{e^{\alpha t} - 1}{1 + \beta e^{\alpha t}}$$



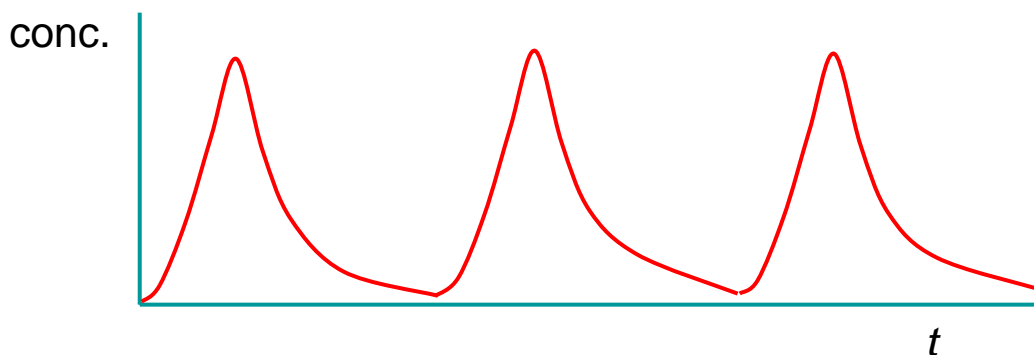


# Oscillations in Gas Phase Kinetics

Consider the concentration profile of an intermediate in the  $\text{H}_2 + \text{O}_2$  reaction.



What if more reactant is supplied?



Examples:

Flaring of phosphorus in a loosely stoppered flask

(Robert Boyle, 17th century)

Cool flames = limited combustion of hydrocarbons due to "long-lived" intermediates which damp the explosion.

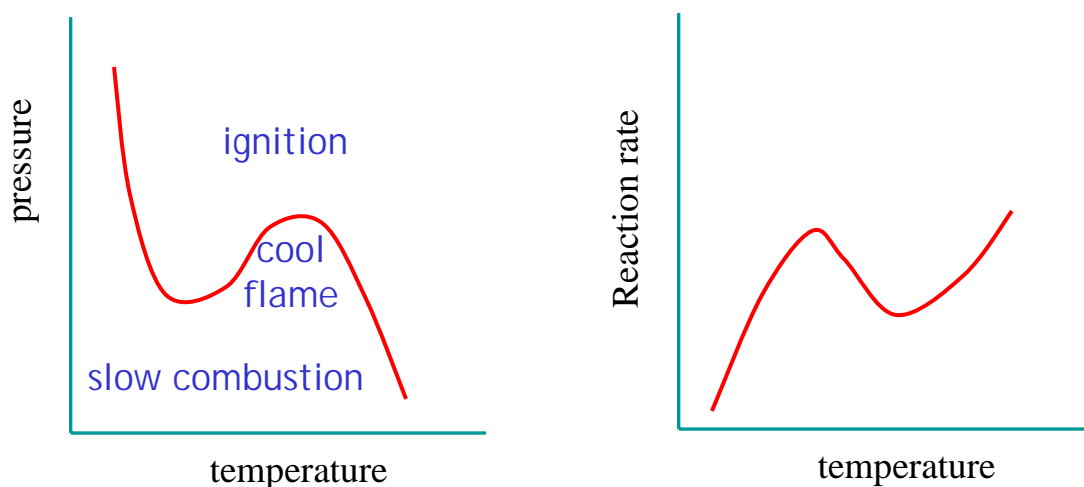
Pre-ignition (autoignition) producing "knock" in auto engines.

# Cool Flame Oscillations

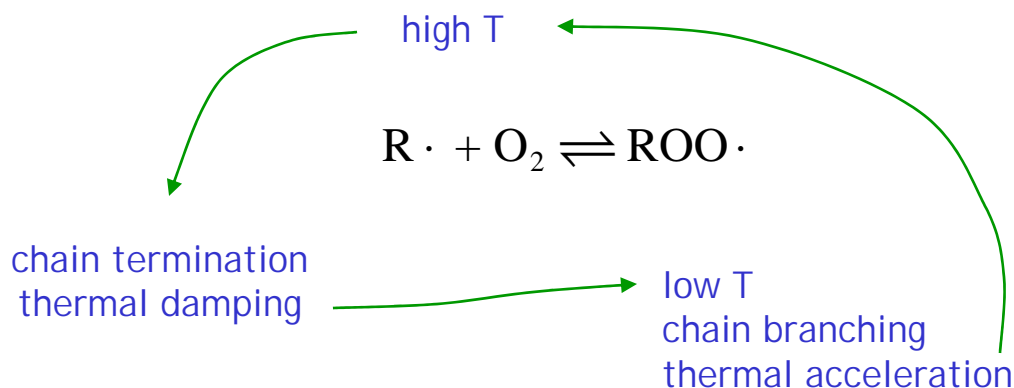
Hydrocarbon fuels spontaneously ignite in the presence of  $O_2$  at  $T > 400-500$  K.

"True" ignition gives  $CO$ ,  $CO_2$ ,  $H_2O$  and  $T$  increases  $\sim 1000$  K.

"Cool" flames produce  $ROH$ ,  $RCHO$ ,  $RCOOH$  and  $\Delta T \sim 100$  K

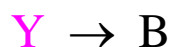
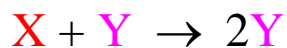
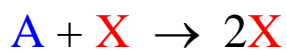


Oscillations occur because of both chemical and thermal feedback.

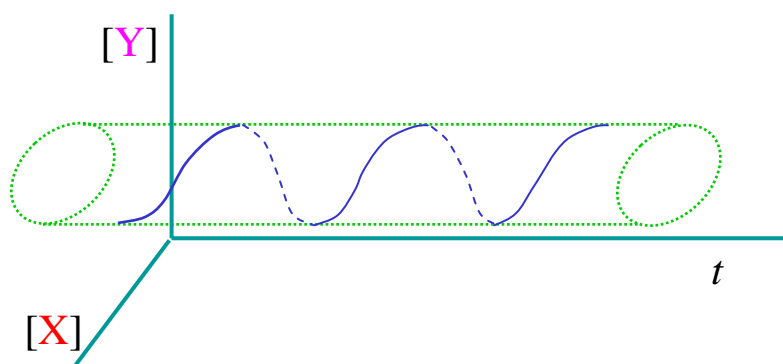
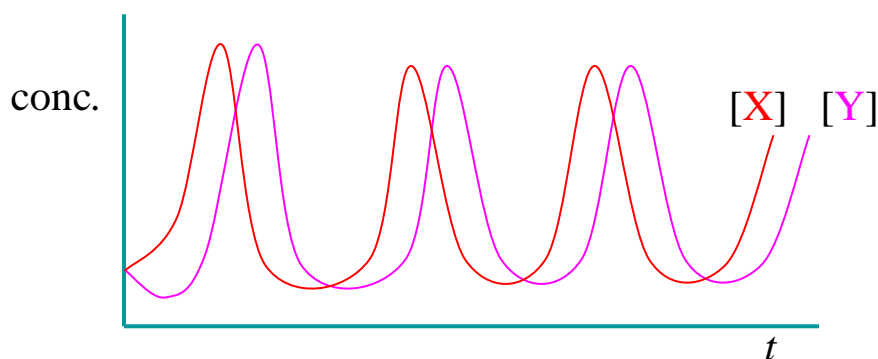


# Oscillating Reactions

## The Lotka-Volterra Mechanism

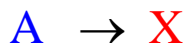


[A] is held constant (replenished). [X] and [Y] oscillate.

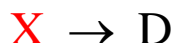
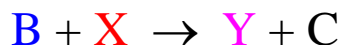


# Oscillating Reaction Models

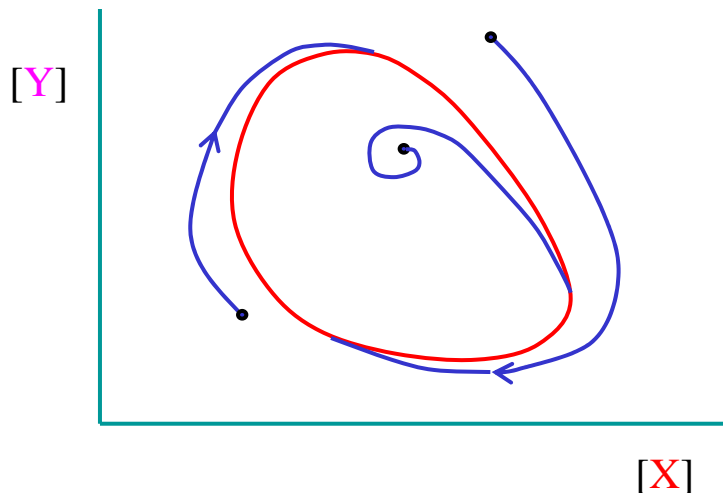
Brusselator



Prigogine *et al*

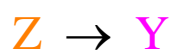
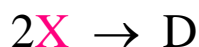
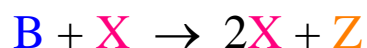


[A] and [B] are held constant. [X] and [Y] settle down to a **limit cycle**:

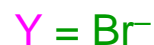


Oregonator

Noyes *et al*



The B-Z reaction is of this general form, with



18 steps, 21 species!