

Lecture 3

Recap – Lecture 2

- Global reaction rate is typically empirical

- Elementary reaction rate is given by Law of Mass action $k \prod_{i=1}^N [R_i]^{a_i}$

- Rate constant - Arrhenius rate – energetic collisions are required

- Full mechanism is very large and complex

- Types of reactions

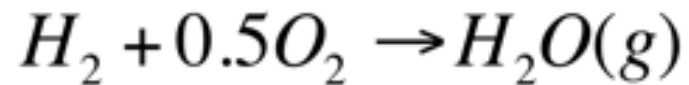


- Simplification possible: steady state and equilibrium approximations
 - NO formation as an example

Dissociation & Equilibrium (Ch. 3)

- Introduce dissociation and equilibrium concepts
- Calculate equilibrium composition of combustion products
 - through simple examples
- Practical relevance of equilibrium calculation/composition

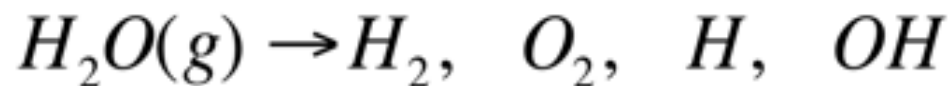
Dissociation & Equilibrium



Space shuttle engine combustion

$$\left[\sum_{i=1}^N n_i \bar{h}_i(T_{in}) \right]_{reac} + Q = \left[\sum_{i=1}^N n_i \bar{h}_i(T_f) \right]_{prod} \quad \Rightarrow \quad T_f \approx 5800 \text{ K}$$

Experimental value $T_f \approx 3600 \text{ K}$, where is the disconnect?



Dissociation reaction – endothermic

Products of hydrocarbon combustion will usually have CO and H₂
=> Incomplete combustion

How to determine the product composition?

Chemical equilibrium

2nd law : maximum entropy or minimum Gibbs free energy at equilibrium

$$dG_{mix}=0 \text{ at constant } P, T$$

$$G_{mix} = H_{mix} - TS_{mix}$$

$\dot{\omega}_i = 0$ for all species
for chemical kinetics

$$G_{mix} = \sum_{i=1}^N n_i \bar{g}_i$$

$$\bar{g}_i = \bar{g}_i^0 + R^0 T \ln(P_i / P^0)$$

(T, $p_0 = 1$ bar)

$$dG_{mix} = \sum_{i=1}^N \bar{g}_i dn_i + \sum_{i=1}^N n_i d\bar{g}_i = 0$$

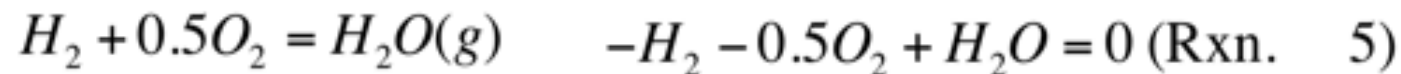
This part goes to 0, because T, P are const.

dn_i are related through stoichiometric coefficients

$$dn_{R1} = -(\omega V) a_1, dn_{R2} = -(\omega V) a_2, dn_{P1} = (\omega V) b_1, dn_{P2} = (\omega V) b_2$$

Equilibrium constant

$$-\frac{\Delta G^0}{R^0T} = \ln \left[\frac{(P_{P1}/P^0)^{b_1} (P_{P2}/P^0)^{b_2} \dots}{(P_{R1}/P^0)^{a_1} (P_{R2}/P^0)^{a_2} \dots} \right] \quad \Leftrightarrow \quad -\frac{\Delta G^0}{R^0T} = \ln K_p$$

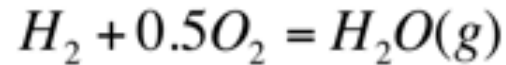


$$K_p = \frac{(P_{H_2O}/P_o)}{(P_{H_2}/P_o)(P_{O_2}/P_o)^{1/2}}$$

$$K_p = \frac{X_{H_2O}}{X_{H_2}X_{O_2}^{1/2}} \left(\frac{P_o}{P} \right)^{1/2} = K_x \left(\frac{P_o}{P} \right)^{1/2}$$

$$K_p = K_c \left(\frac{P_o}{R^0T} \right)^{1/2} = \frac{k_f}{k_b} \left(\frac{P_o}{R^0T} \right)^{1/2}$$

Further comments



$$K_p = \frac{X_{H_2O}}{X_{H_2}X_{O_2}^{1/2}} \left(\frac{P_o}{P} \right)^{1/2} = K_x \left(\frac{P_o}{P} \right)^{1/2}$$

$P \uparrow \Rightarrow$ less dissociation, Rxn goes to the right

$T \uparrow \Rightarrow$ more dissociation, Rxn goes to the left

Principle of Le Chatelier –

If conditions change, equilibrium point shifts to minimise the change.

- Usage
for fuel rich combustion – use water-gas shift reaction
$$\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$$
- Refinement of T_f calculation
complex calculation – codes are available,
see internet based learning
$$\left[\sum_{i=1}^N n_i \bar{h}_i(T_{in}) \right]_{\text{reac}} + Q = \left[\sum_{i=1}^N n_i \bar{h}_i(T_f) \right]_{\text{prod}}$$
- Are combustion products in practice in equilibrium?
No & Yes

- At high T , dissociation is inevitable \Rightarrow lowering of product temperature
- Dissociation and other reactions can be in equilibrium, where $\Delta s = 0$ (maximum entropy), $\Delta g = 0$ (minimum Gibbs free energy)
- Equilibrium constant – depends only on T , discussed Principle of Le Chatelier
- Atom conservation & Equilibrium constant relation give product composition at equilibrium – purely thermodynamics
- Rate of reaction \Rightarrow Chemical Kinetics, which also need thermodynamics – backward rate constants

Reaction possible or impossible?

- II law of thermodynamics $\Rightarrow ds > 0$ for a natural process
- from thermodynamics, Gibbs free energy **$dg = dh - Tds$**
- for a natural process $dg < 0$; $dg = 0$ at equilibrium

No	h	s	g	Remark
1	-	+	-	Possible at all T (also exothermic)
2	-	-	-/+	Possible at low T; impossible at high T
3	+	+	-/+	Possible at high T; impossible at low T
4	+	-	+	Impossible at all T

$\text{N}_2 + 0.5 \text{O}_2 \longrightarrow \text{N}_2\text{O}$ is this possible at $T=300\text{K}$ & $P=1.0 \text{ atm}$?

$\text{H}_2\text{O(l)} \longrightarrow \text{H}_2\text{O}$ at what T does this reaction occur for $P = 1.0 \text{ atm}$?

Lecture 4

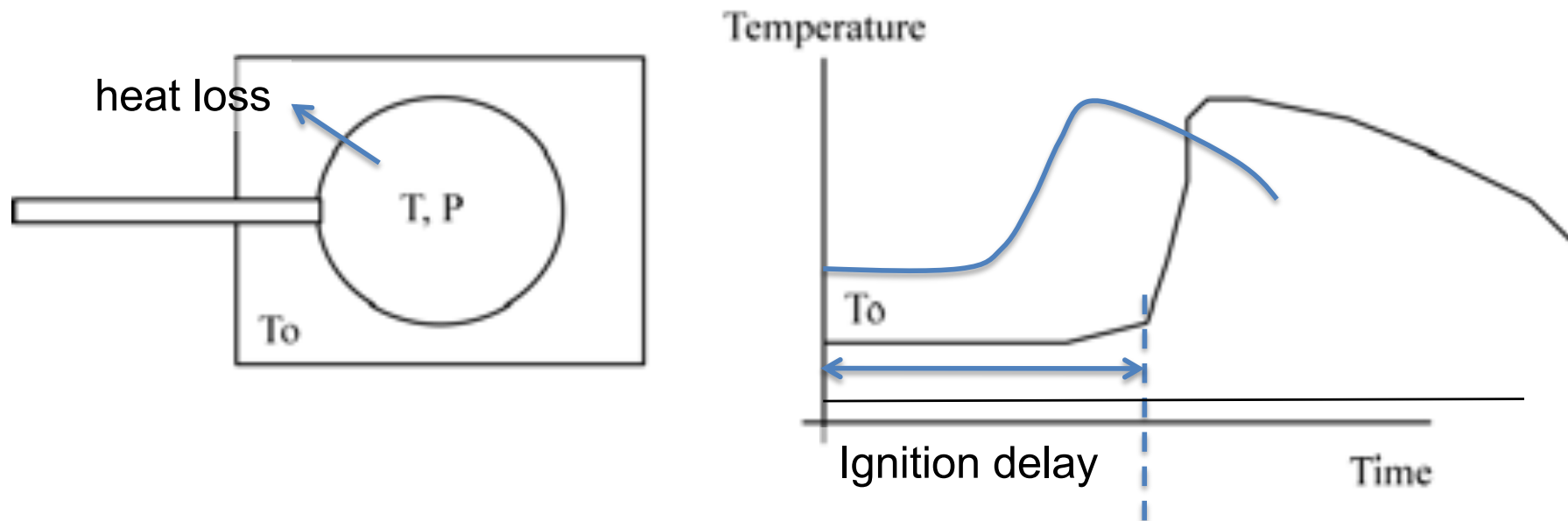
Limit phenomena – Ignition (Ch. 4) & Extinction (Ch. 5)

- Characterised multi-component mixture and defined equivalence ratio, AFR, stoichiometry relations, T_f , governing equations - L1
- Law of mass action, reaction rate expression, Elementary vs global reactions - L2
- At high T , dissociation is inevitable \Rightarrow equilibrium compositions, devised methods to compute the equilibrium composition, Principle of Le Chatelier – L3
- Today, look at autoignition phenomenon (also extinction)

- Nature and application of autoignition – What is autoignition?
- One-step chemical model and conserved scalar
- Predict autoignition time without heat loss
- Effects of heat loss
- Practical consequences

What is autoignition?

- Self ignition or spontaneous ignition



How to predict this time?

Conserved scalars

Fuel + ν Air \rightarrow Products

$$\frac{d[F]}{dt} = -A \exp\left(-E/R^0T\right) \left(\frac{\rho Y_{fu}}{MW_{fu}}\right) [Ox] \Leftrightarrow \dot{w}_{fu} = -A \frac{MW_{fu}}{MW_{fu} MW_{ox}} \rho^2 Y_{fu} Y_{ox} \exp(-E/R^0T)$$

$$\rho \frac{\partial Y_{fu}}{\partial t} + \rho U \frac{\partial Y_{fu}}{\partial x} = \frac{\partial}{\partial x} \left(\rho D \frac{\partial Y_{fu}}{\partial x} \right) + \dot{w}_{fu} \quad \rho c_p \frac{\partial T}{\partial t} + \rho c_p U \frac{\partial T}{\partial x} = \frac{\partial}{\partial x} \left(\lambda \frac{\partial T}{\partial x} \right) - Q \dot{w}_{fu}$$

Z, conserved scalar

$$\rho \frac{\partial (QY_{fu} + c_p T)}{\partial t} + \rho U \frac{\partial (QY_{fu} + c_p T)}{\partial x} = \frac{\partial}{\partial x} \left(\rho D \frac{\partial (QY_{fu} + c_p T)}{\partial x} \right)$$

For homogeneous case:

$$QY_{fu} + c_p T = \text{const.} = QY_{fu,0} + c_p T_0$$

Constant volume combustion?

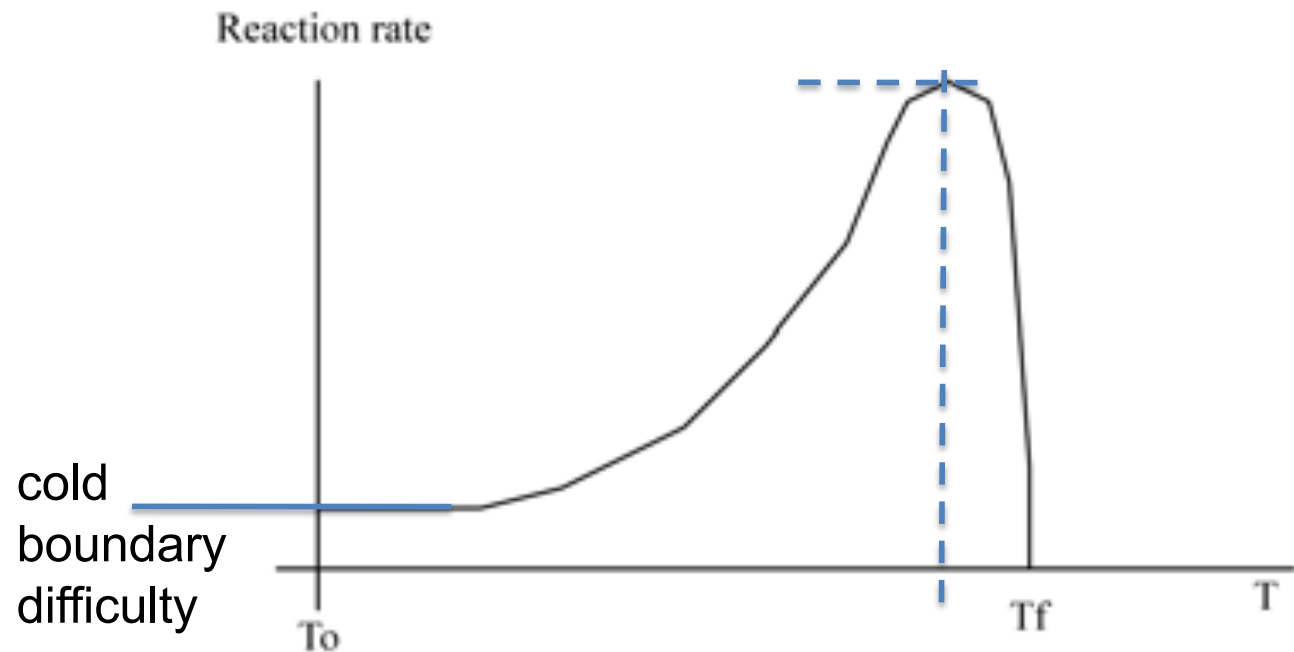
$$Y_{ox} = Y_{ox,0} - S c_p (T - T_0) / Q \quad S = \nu MW_{air} / MW_{fuel}$$

Flame Temperature & Rxn. rate

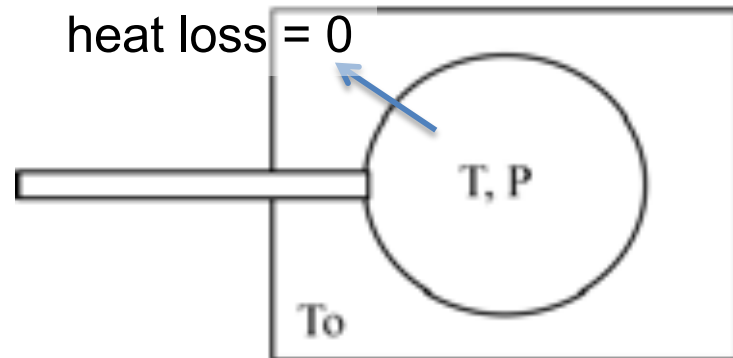
$$QY_{fu} + c_p T = \text{const.} = QY_{fu,0} + c_p T_0 \quad Y_{fu} = 0 \Rightarrow T_f = Y_{fu,0} Q / c_p + T_0$$

$$\dot{w}_{fu} = -A \frac{MW_{fu}}{MW_{fu} MW_{ox}} \rho^2 Y_{fu} Y_{ox} \exp(-E / R^0 T)$$

$$-\dot{w}_{fu} = C f(T)$$



Autoignition without heat loss



$$Y_{fu} = Y_{fu,0} - c_p(T - T_0)/Q$$

$$\rho c_p \frac{\partial T}{\partial t} = Q \frac{MW_{fu}}{MW_{fu} MW_{ox}} \rho^2 A Y_{fu} Y_{ox} \exp(-E/R^0 T)$$

$$Y_{ox} = Y_{ox,0} - S c_p(T - T_0)/Q$$

$$\frac{\partial T}{\partial t} = B \exp(-E/R^0 T) \quad T = T_0 + \Delta T = T_0 \left(1 + \frac{\Delta T}{T_0}\right) \Rightarrow \frac{E}{R^0 T} = \frac{E}{R^0 T_0 (1 + x)}$$

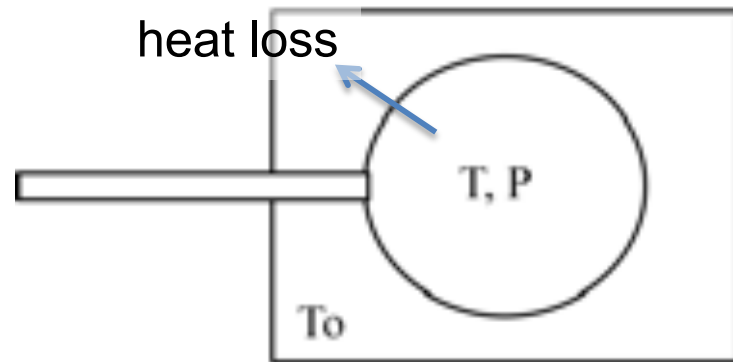
$$\frac{\partial T}{\partial t} = B \exp\left(-\frac{E}{R^0 T_0}\right) \exp\left[\frac{E(T - T_0)}{R^0 T_0^2}\right]$$

$$t = \frac{1}{B} \frac{R^0 T_0^2}{E} \exp\left(\frac{E}{R^0 T_0}\right) \left(1 - \exp\left[-\frac{E(T - T_0)}{R^0 T_0^2}\right]\right)$$

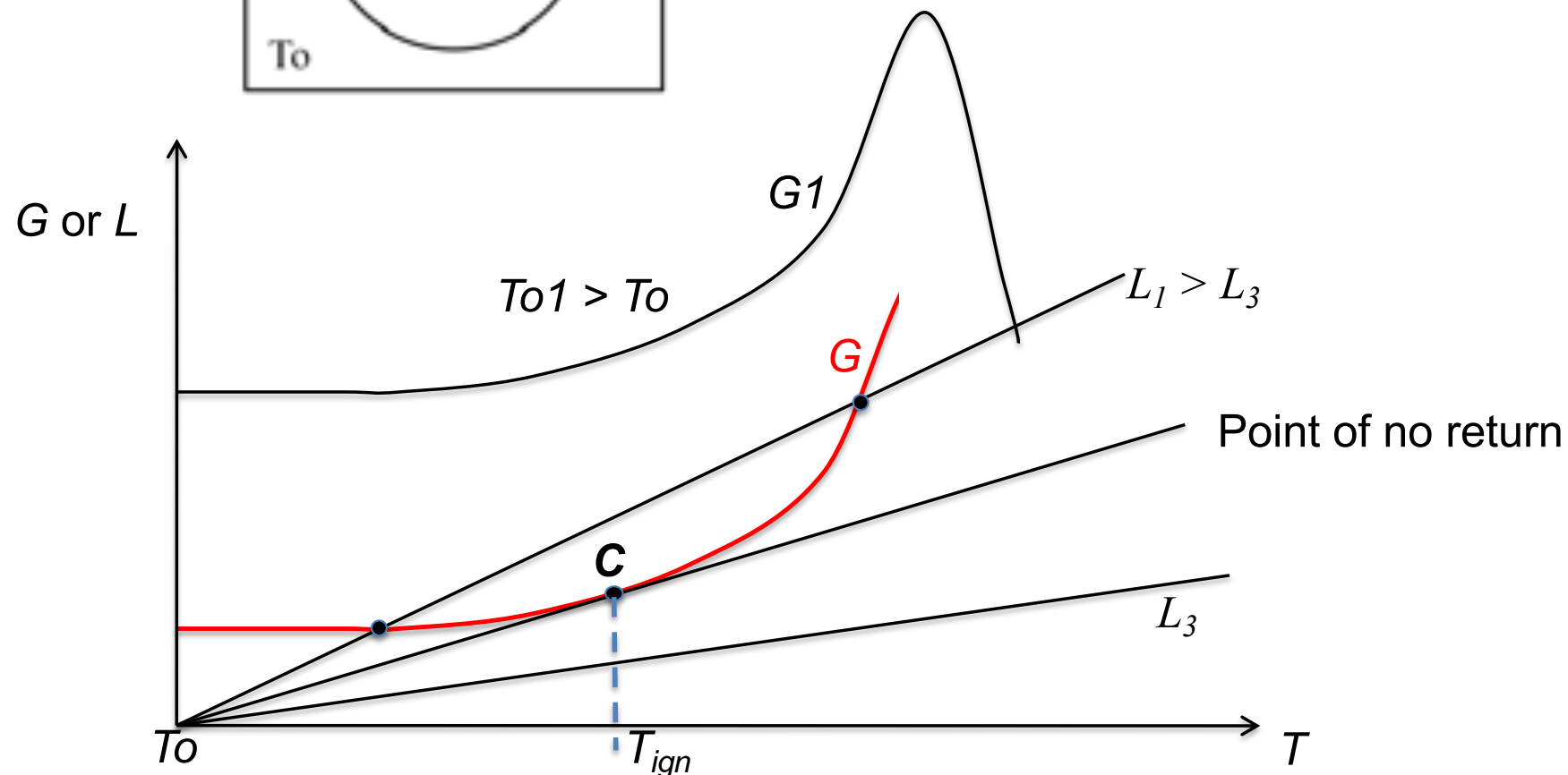
$$\tau_{ign} = \left(\frac{Q}{c_p} \frac{MW_{fu}}{MW_{fu} MW_{ox}} \rho_0 A Y_{fu,0} Y_{ox,0} \right)^{-1} \frac{R^0 T_0^2}{E} \exp\left(\frac{E}{R^0 T_0}\right)$$

Effects of T_0 , p , Y_{fu} , Y_{Ox0} ?

With heat losses



$$\frac{\partial T}{\partial t} = \frac{1}{\rho c_v} Q \dot{w}_{fu} - \frac{A_V}{V \rho c_v} h(T - T_0) = G - L$$



Autoignition Temperature

$$\left. \begin{array}{l} \text{At C, } G = L \\ \frac{\partial G}{\partial T} = \frac{\partial L}{\partial T} \end{array} \right\} \quad T_{ign}^2 - \cancel{\frac{E}{R^0}} T_{ign} + \frac{E}{R^0} T_0 = 0$$

$$T_{ign} = \frac{T_a - \sqrt{T_a^2 - 4T_a T_0}}{2}$$

$$T_{ign} = \frac{T_a}{2} \left[1 - \sqrt{1 - 4T_0/T_a} \right]$$

$$\sqrt{(1-x)} = 1 - x/2 - x^2/8 - \dots$$

$$T_{ign} \approx T_0 + \frac{T_0^2}{T_a}$$

Alternative method,
see Ex. 4-2 in page
Ch4/9

Pres. versus Tign.?

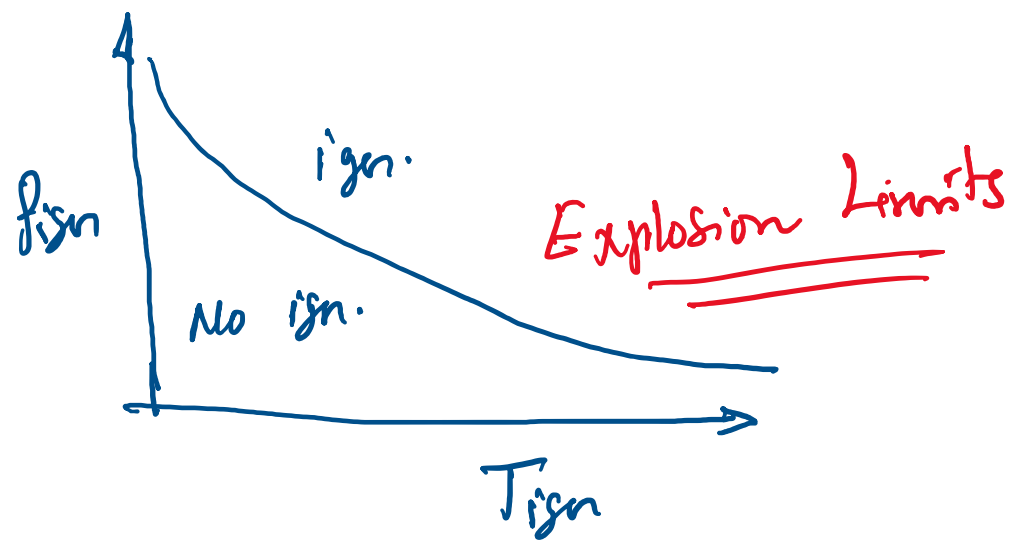
Practical relevance?

Spark ignition?

$$\frac{\partial Q_L}{\partial T} = \frac{\partial G}{\partial T}$$

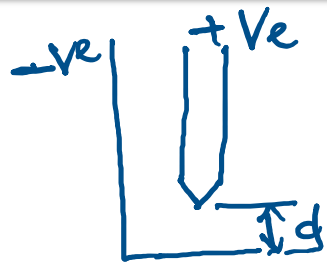
$$\frac{hA}{V} = Q A_f \cancel{\delta^2} \gamma_f \gamma_o \exp\left(-\frac{T_a}{T_{ign}}\right) \frac{T_a}{T_{ign}^2}$$

$$\Rightarrow P_{ign} = f(\dots, T_{ign})$$



Also,
Chain branching
Vs.
Chain termination
Reaction rates
play important role.

SPARK IGNITION



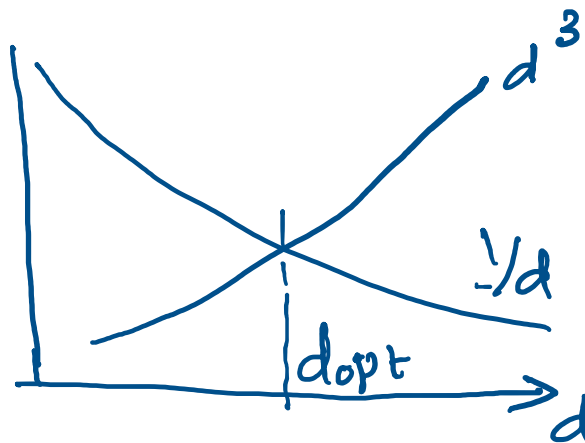
$$\rho C_p V \frac{\partial T}{\partial t} = \dot{G} - \dot{L} + \dot{Q}_{\text{spark}}$$

$$\text{@ } t=0 \quad \dot{G} \approx 0, \quad \int_0^{t_{\text{spark}}} dt$$

$$\Rightarrow \rho C_p V (T_f - T_0) + \cancel{L} \approx Q_{\text{spark}}$$

(A/V)

$$V \sim d^3; \quad L \sim 1/d$$



$$Q_{\text{spark}} \sim 0.2 \text{ to } 0.5 \text{ mJ for H.C.}$$

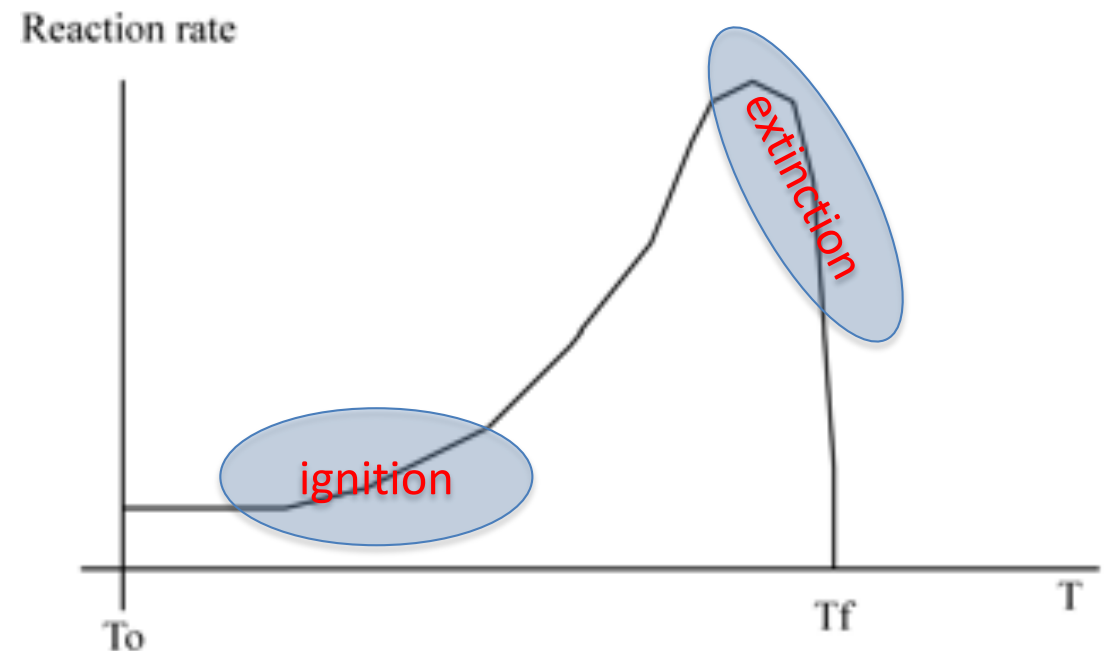
$$0.02 \text{ mJ for H}_2$$

$$\text{C}_2\text{H}_2$$

- Autoignition – related to safety issues
- Fuel consumption and temperature rise are related in adiabatic systems → conserved scalar
- Most fuels have high T_a and thus temperature rise before ignition is small
- Ignition delay time, τ_{ign} – used linearisation method for adiabatic systems
- τ_{ign} decreases very fast with T_0 , varies as $1/p$
- In non-adiabatic systems, excessive heat loss avoids autoignition, $L = G$ at autoignition

Lecture 5:

Ch. 5: Limit phenomena (Extinction)



- Autoignition – related to safety issues
- Fuel consumption and temperature rise are related in adiabatic systems \rightarrow conserved scalar
- Most fuels have high T_a and thus temperature rise before ignition is small
- Ignition delay time, τ_{ign} , estimates
- τ_{ign} decreases very fast with T_0 , varies as $1/p$
- In non-adiabatic systems, excessive heat loss avoids autoignition, $L = G$ at autoignition

- Model problem & its theory for extinction
 - Well Stirred Reactor (WSR)
- Explain the phenomenon of flame extinction

Model reactors:

1) Batch reactor (PSR)



$$\frac{dm_i}{dt} = \dot{w}_i;$$

$$\rho C_p \frac{dT}{dt} = \dot{Q}$$

$$\neq P = \rho RT$$

$$m_i = \rho V_i \Rightarrow \frac{dY_i}{dt} = \frac{\dot{w}_i}{\rho} - Y_i \frac{d \ln \rho}{dt}$$

2) CSTR or WSR:



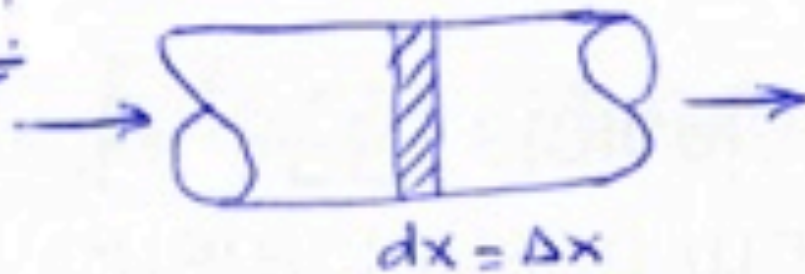
$$\frac{dm_i}{dt} = \dot{m}_{i,out} - \dot{m}_{i,in} + \int \dot{w}_i dv$$

Steady state:

$$\dot{m}_{i,out} - \dot{m}_{i,in} = \int \dot{w}_i dv = \underline{\underline{\dot{w}_i V}}$$

$$(Y_{i,out} - Y_{i,in}) = \dot{w}_i \left(\frac{V}{\dot{m}} \right)$$

3) PFR!

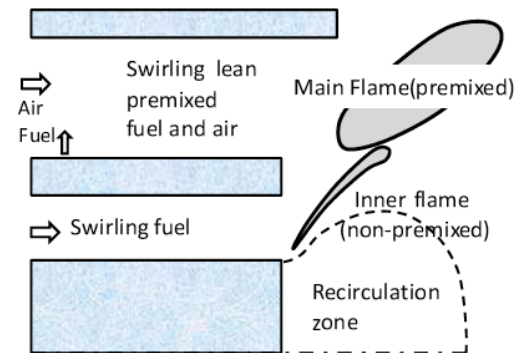
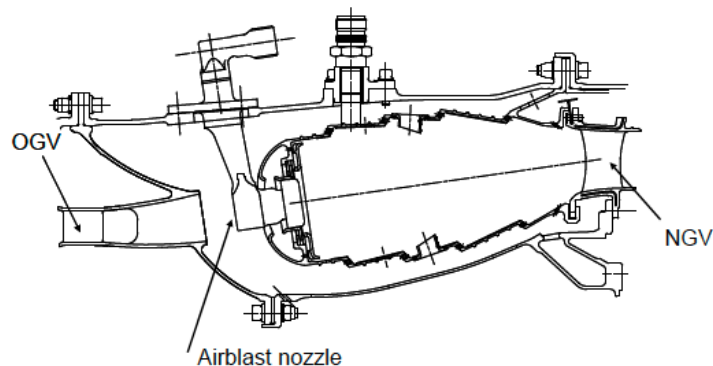


$$A \Delta x \frac{dm_i}{dt} = \Delta m_i A + \dot{w}_i A \Delta x$$

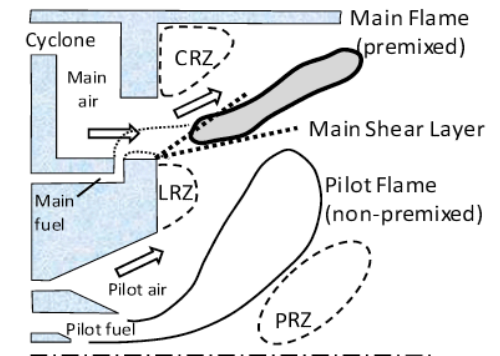
$$\frac{dm_i}{dt} = \frac{\Delta m_i}{\Delta x} + \dot{w}_i \Rightarrow \text{Steady State} \quad \boxed{\frac{dm_i}{dx} = \dot{w}_i}$$

Typical main & after burners – Examples for WSR model

RRD BR Series Combustor
(Courtesy of Rolls-Royce Deutschland)

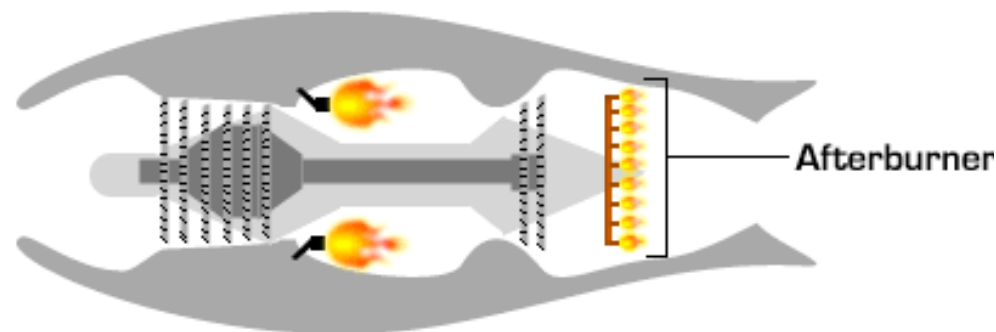


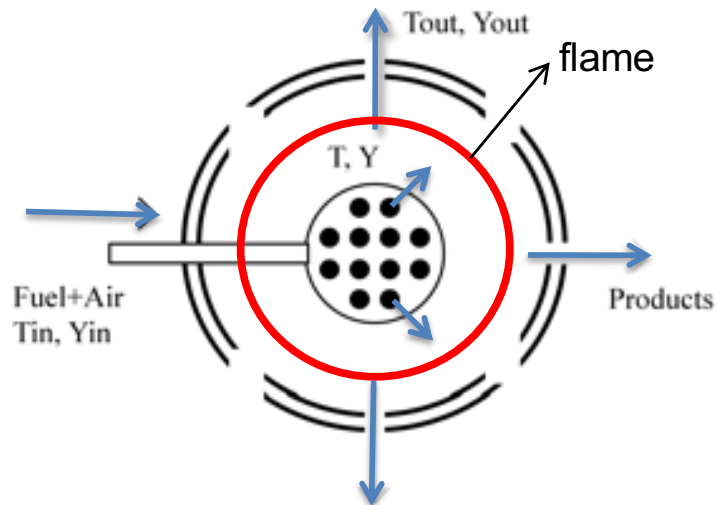
(b) DLN for gaseous fuel



(d) TAPS for liquid fuel

(taken from Turbulent Premixed Flames,
N. Swaminathan & KNC. Bray (Eds.), CUP, 2011)





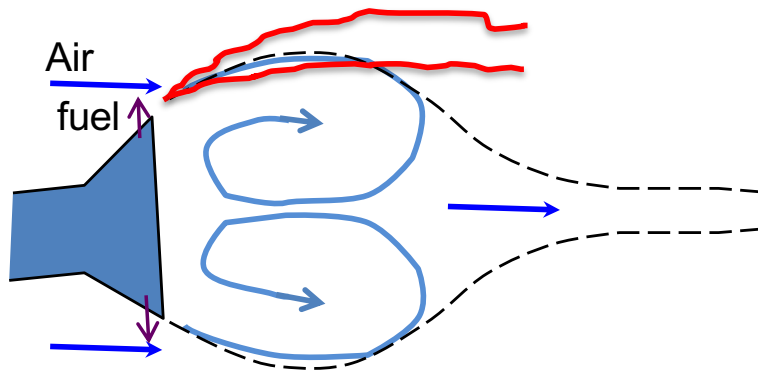
Assumptions:

- homogeneous, steady
- $T_{out} = T$, $Y_{i,out} = Y_i$, adiabatic
- one step chemistry, $c_p = \text{const}$

$$\dot{m} (Y_{i,out} - Y_{i,in}) = \dot{w}_i V$$

$$\dot{m} c_p (T_{out} - T_{in}) = -\dot{w}_{fu} V Q$$

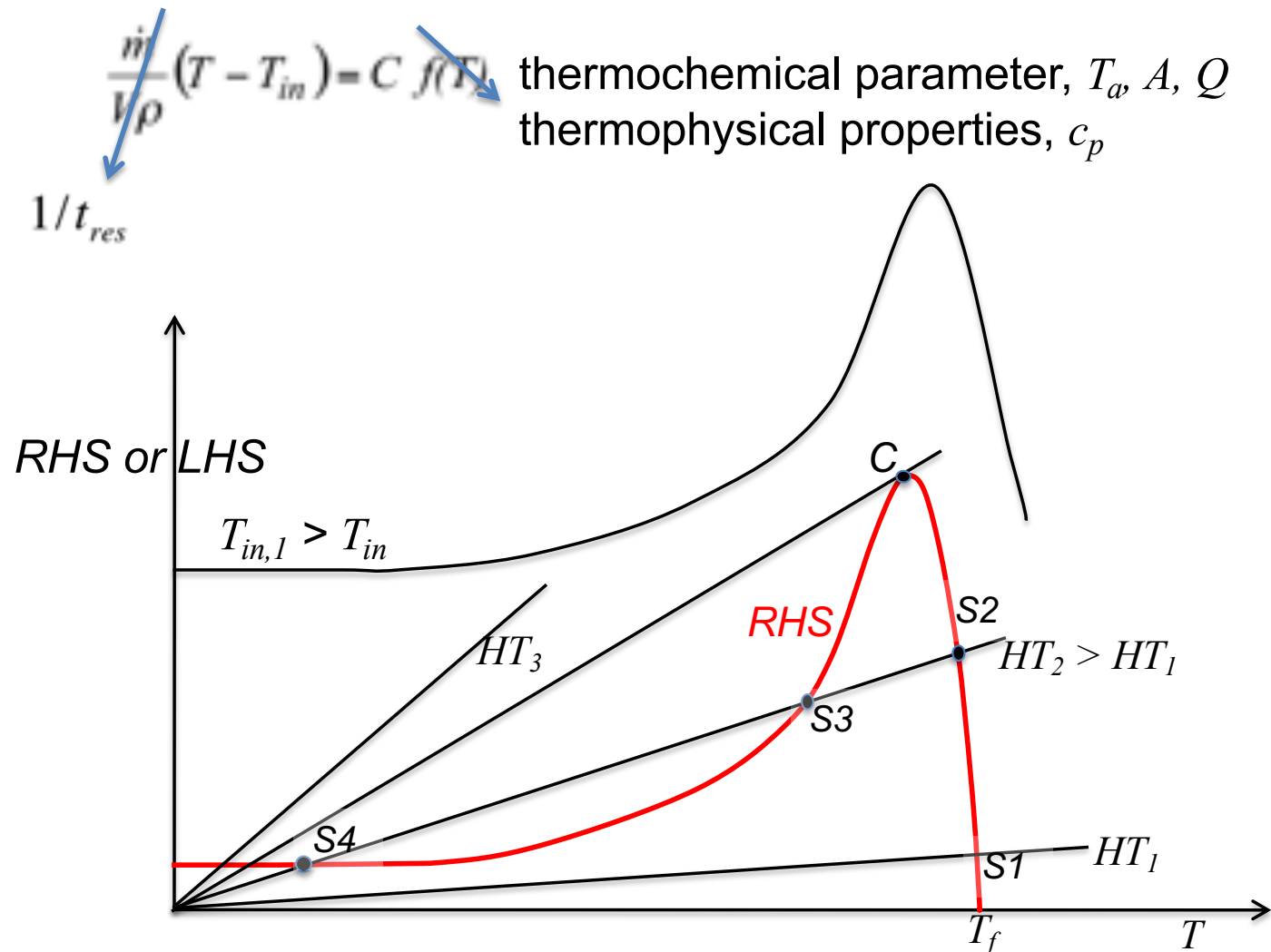
$$\dot{w}_{fu} = -A \frac{MW_{fu}}{MW_{fu} MW_{ox}} \rho^2 Y_{fu} Y_{ox} \exp(-E/R^0 T)$$

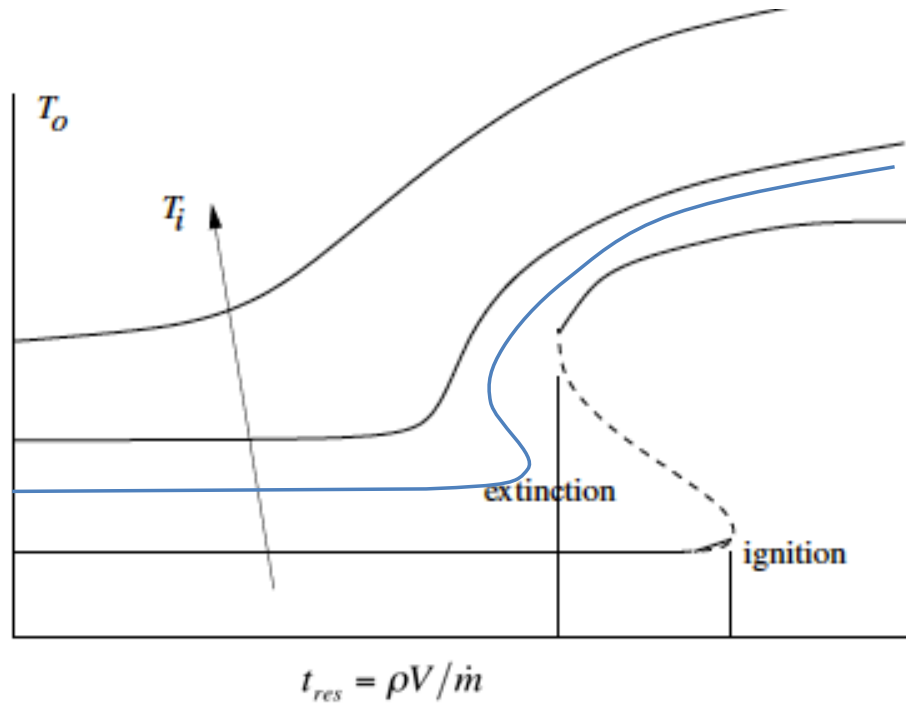


$$Y_{fu} = Y_{fu,in} - c_p (T - T_{in}) / Q$$

$$Y_{ox} = Y_{ox,in} - S c_p (T - T_{in}) / Q$$

$$\rho = \frac{P \overline{MW}}{R^0 T}$$

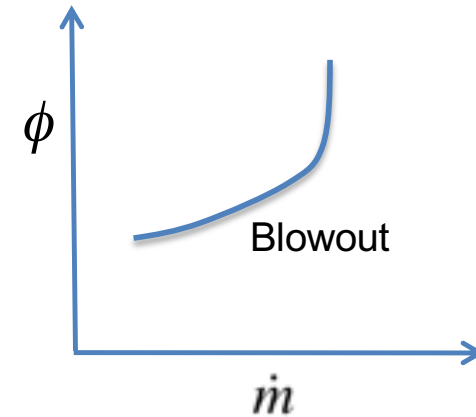
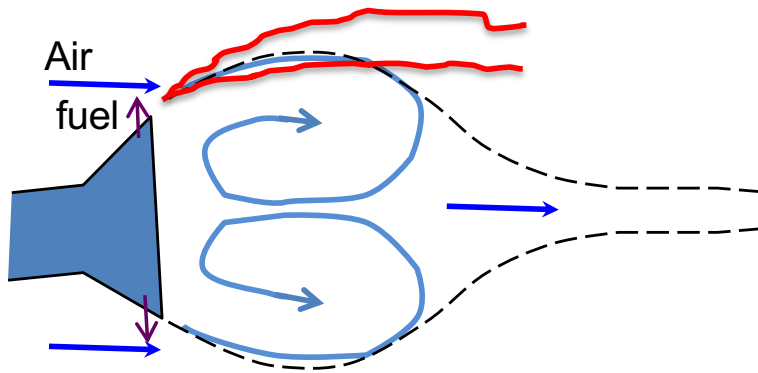




Same information as in the previous slide,
in a different form

Practical importance

- Flame stabilisation



- Flame extinction at high altitudes (engine flame-out)!
- Chemical process industries – Reaction or no reaction

- WSR – idealisation of combustion in many practical devices
- Competition between reaction time and residence time $\Rightarrow T$ of the reactor
- No combustion if the residence time is too short
- WSR – approximates the characteristics of practical flame stabilisers and trends are well represented