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# Deflagrations

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# **Deflagration - laminar flame**

A flame is a thin region in space where chemical reactions convert a fuel-air mixture into combustion products.



A hydrogen flame produces very little light due to absence of carbon

#### **Deflagration- turbulent flame**







Shutter Speed Settings F-stop – 5.6

https://sites.google.com/site/srcombexp/home/visualizing-flames

# Explosions



# US Bureau of Mines coal mine explosion test

# Outline

- First Law of Thermodynamics for combustion
  - heat of combustion
  - adiabatic flame temperature
  - constant volume pressure
- Laminar flames
  - chemical kinetics
  - laminar burning velocity
  - flame quenching
  - flame instabilities
- Turbulent flames
  - turbulent combustion regimes

## **First Law Analysis for Reacting System**

Consider a constant pressure process in which  $n_f$  moles of fuel react with  $n_a$  moles of air to produce  $n_p$  moles of product:



Applying First Law with state 1 being the reactants at  $P_1$ ,  $T_1$  and state 2 being products at  $P_2$ ,  $T_2$ :

$$Q = \Delta U + W$$

$$Q_{1\to 2} = (U_2 - U_1) + P(V_2 - V_1)$$

#### **First Law Analysis for Reacting System**

$$Q = (U_2 - U_1) + P(V_2 - V_1)$$

$$= (U_2 + P_2 V_2) - (U_1 + P_1 V_1)$$

$$=H_2-H_1$$

$$= H_P - H_R = \sum_P n_i \overline{h_i}(T_p) - \sum_R n_i \overline{h_i}(T_R)$$

 $H_P < H_R$  Q < 0 exothermic reaction  $H_P > H_R$  Q > 0 endothermic reaction

#### **Enthalpy of Reaction**

Consider the case where the final temperature of the products is the same as the initial temperature of the reactants (e.g., calorimeter is used to measure Q).



The heat released under this situation is referred to as the enthalpy of reaction,  $\Delta H_R$ ,

$$\Delta H_R = \sum_P n_i \overline{h_i}(T_p) - \sum_R n_i \overline{h_i}(T_R)$$
  
=  $\sum_P n_i \overline{h_i}(T_o) - \sum_R n_i \overline{h_i}(T_o)$  units : kJ per kg or kmol of fuel

#### Enthalpy of the i'th component in a mixture

$$\overline{h_i}(P,T) = \overline{h_{f,i}^o} + [\overline{h_i}(P,T) - \overline{h_i}(1atm,298K)]$$
  
chemical enthalpy sensible enthalpy =  $\int_{298K}^T c_{p,i} dT$ 

By international convention, the enthalpy of every element in its natural state (e.g.,  $O_2(g)$ ,  $N_2(g)$ ,  $H_2(g)$ , C(s)) at STP has been set to zero

i.e, 
$$h(1atm, 298K) = h_f^o = 0$$
 (note the notation convention)  
at STP

# **Heat of Formation for Different Fuels**

FUEL		h <sup>o</sup> <sub>f</sub> (mJ/kmol)
C <sub>2</sub> N <sub>2</sub> (g)	Cyanogen	309.1
H <sub>2</sub> (g)	Hydrogen	0.0
NH <sub>3</sub> (g)	Ammonia	-45.7
CH4 (g)	Methane	-74.9
C <sub>3</sub> H <sub>8</sub> (g)	Propane	-103.9
C <sub>2</sub> H <sub>17</sub> (1)	Gasoline <sup>2</sup>	-305.6
$C_{8}H_{18}(l)$	Octane	-249.5
C <sub>5</sub> H <sub>15</sub> (1)	Isooctane	-259.3
C14.4H24.9 (1)	Diesel <sup>2</sup>	-174.0
C <sub>15</sub> H <sub>32</sub> (1)	Pentadecane	-428.9
$C_2H_2$ (g)	Acetylene	226.7
C <sub>6</sub> H <sub>6</sub> (1)	Benzene	48.91
$C_{10}H_{8}$ (s)	Naphthalene	78.1
CH,O (1)	Methanol	-239.1
C2H6O (1)	Ethanol	-277.2
CH <sub>3</sub> NO <sub>2</sub> (1)	Nitromethane	-113.1
C (s)	Graphite	0.0
$C_{126}H_{144}O_8N_3$ (s)	Good coal <sup>2</sup>	-10000.0



#### The data can be found in the JANNAF tables

#### Heat of Combustion

The maximum amount of energy is released from a fuel when reacted with a stoichiometric amount of air and all the hydrogen and carbon contained in the fuel is converted to  $CO_2$  and  $H_2O$ 

$$C_{\alpha}H_{\beta} + \left(\alpha + \frac{\beta}{4}\right)(O_2 + 3.76N_2) \rightarrow \alpha CO_2 + \frac{\beta}{2}H_2O + 3.76\left(\alpha + \frac{\beta}{4}\right)N_2$$

This maximum energy is referred to as the **heat of combustion** or the **heating value** and it is typically given per mass of fuel

	FUEL	∠H <sub>R</sub> (298K){MJ/kg	j)
$\overline{C_2N_2(g)}$	Cyanogen	21.0	
$H_{2}(g)$	Hydrogen	141.6 🗲	
$NH_3(g)$	Ammonia	22.5	15
$CH_4(g)$	Methane	55.5	
$C_{3}H_{8}(g)$	Propane	50.3	
$C_8H_{18}(l)$	Octane	47.9	
$C_{15}H_{32}(l)$	Pentadecano	47.3	hydrocarbons
$C_{20}H_{40}(g)$	Eicosane	47.3	
$C_{2}H_{2}(g)$	Acetylene	49.9	
$C_{10}H_8(s)$	Naphthalene	40.3	
$CH_4O(l)$	Methanol	22.7	
$C_2 H_6 O(l)$ .	Ethanol	29.7	alcohols
$CH_3NO_2(l)$	Nitromethan	ie 11.6	

There are two possible values for the heat of combustion depending on whether the water in the products is taken to be saturated liquid or vapour.



 $\Delta H_R = H_P - H_R < 0$  (exothermic)

The term **higher heat of combustion** is used when the water in the products is taken to be in the liquid state ( $h_{H20} = h_f$ )

The term **lower heat of combustion** is used when the water in the products is taken to be in the vapour state ( $h_{H20} = h_g$ )

#### Heat of Combustion, graphical



#### **Adiabatic Flame Temperature**

Consider the following adiabatic constant pressure process:



For a constant pressure process, the final products temperature,  $T_a$ , is known as the **adiabatic flame temperature** (AFT).

$$Q = \sum_{P} n_i \overline{h_i}(T_p) - \sum_{R} n_i \overline{h_i}(T_R) = 0$$
$$\sum_{P} n_i \overline{h_i}(T_a) = \sum_{R} n_i \overline{h_i}(T_1)$$

For a given reaction where the  $n_i$ 's are known for both the reactants and the products,  $T_a$  can be calculated explicitly.

# **Adiabatic Flame Temperature**

$$\sum_{P} n_i \overline{h_i}(T_a) = \sum_{R} n_i \overline{h_i}(T_1)$$

$$\sum_{P} n_i \left[\overline{h_{f,i}^o} + \left(\overline{h_i}(T_a) - \overline{h_i}(298K)\right)\right] = \sum_{R} n_i \left[\overline{h_{f,i}^o} + \left(\overline{h_i}(T_1) - \overline{h_i}(298K)\right)\right]$$

$$\sum_{P} n_i \left(\overline{h_i}(T_a) - \overline{h_i}(298K)\right) = \sum_{R} n_i \left(\overline{h_i}(T_1) - \overline{h_i}(298K)\right) - \left[\sum_{P} n_i \overline{h_{f,i}^o} - \sum_{R} n_i \overline{h_{f,i}^o}\right]$$
Sensible heat of products
Sensible heat of reactants
(equal to 0 if T\_1 = 298K)
$$\Delta H_R^o$$

# Constant Pressure Adiabatic Flame Temperature with products at equilibrium



#### **Constant Volume AFT**

Consider the case where the piston is fixed and the cylinder is perfectly insulated so the process is adiabatic (Q = 0)



$$Q = \sum_{P} n_i \overline{u}_i(T_p) - \sum_{R} n_i \overline{u}_i(T_R) = 0$$
$$\sum_{P} n_i \overline{u}_i(T_a) = \sum_{R} n_i \overline{u}_i(T_1)$$

Note h = u + pv = u + RT, so

$$\sum_{P} n_i(\overline{h_i}(T_a) - \overline{R}T) = \sum_{R} n_i(\overline{h_i}(T_1) - \overline{R}T)$$

#### **Constant Volume AFT**

$$\sum_{P} n_{i} \left[ \overline{h}_{f,i}^{o} + \left( \overline{h}_{i}(T_{a}) - \overline{h}_{i}(298K) \right) - \overline{R}T_{i} \right] = \sum_{R} n_{i} \left[ \overline{h}_{f,i}^{o} + \left( \overline{h}_{i}(T_{1}) - \overline{h}_{i}(298K) \right) - \overline{R}T_{i} \right]$$

$$\sum_{P} n_{i} \overline{h}_{i}(T_{a}) = \left[ \sum_{R} n_{i} \left( \overline{h}_{i}(T_{1}) - \overline{h}_{i}(298K) \right) \right] - \left[ \sum_{P} n_{i} \overline{h}_{f,i}^{o} - \sum_{R} n_{i} \overline{h}_{f,i}^{o} \right] + \left[ \sum_{P} n_{i} \overline{h}_{i}(298K) \right]$$

$$+ \sum_{P} n_{i} \overline{R}T_{a} - \sum_{R} n_{i} \overline{R}T_{1}$$

Extra term compared to constant pressure AFT (term > 0)

The AFT for a constant volume process is larger than for a constant pressure process (no Pdv work).

#### **Constant Volume Combustion Pressure**

Assuming ideal gas behavior:

$$V_{R} = V_{P}$$

$$\frac{n_{R}\overline{R}T_{R}}{P_{R}} = \frac{n_{p}\overline{R}T_{p}}{P_{p}}$$

$$\frac{P_{p}}{P_{R}} = \left(\frac{n_{p}}{n_{R}}\right)\left(\frac{T_{p}}{T_{R}}\right) \quad \rightarrow \quad \frac{P_{CV}}{P_{i}} = \left(\frac{n_{p}}{n_{R}}\right)\left(\frac{T_{a}}{T_{i}}\right)$$

For large hydrocarbons the mole ratio term is close to one

Stoichiometric hydrogen-air:

$$H_{2} + 0.5(O_{2} + 3.76N_{2}) \rightarrow 1H_{2}O + 1.88N_{2}$$

$$\frac{P_{CV}}{P_{i}} = \left(\frac{n_{p}}{n_{R}}\right) \left(\frac{T_{a}}{T_{i}}\right) = \left(\frac{2.88}{3.38}\right) \left(\frac{2383}{298}\right) = 0.85 \cdot 8.0 = 6.8$$

### **Chemical Equilibrium**

- In general the combustion products of hydrogen consist of more than just  $\rm H_2O,\,O_2$  and  $\rm N_2$ 

• At high temperatures the molecules dissociate to form H, O, OH, NO via the following reactions:

 $H_2 \rightarrow 2H$   $O_2 \rightarrow 2O$   $H_2 + O_2 \rightarrow 2OH$   $O_2 + N_2 \rightarrow 2NO$ 

• The opposite direction reactions are also possible

$$2H \rightarrow H_2$$
  $2O \rightarrow O_2$   $2OH \rightarrow H_2 + O_2$   $2NO \rightarrow O_2 + N_2$ 

• At **equilibrium** the rate of the forward reaction equals the rate of the backward reaction.

$$H_2 \leftrightarrow 2H \qquad O_2 \leftrightarrow 2O \qquad H_2 + O_2 \leftrightarrow 2OH \qquad O_2 + N_2 \leftrightarrow 2NO$$

#### **Chemical Equilibrium**

Consider an adiabatic, constant volume ( $\Delta U=0$ ) reaction of  $H_2$ 

$$H_2 + \frac{1}{2}O_2 \to (1 - \alpha)H_2O + \alpha H_2 + \frac{\alpha}{2}O_2$$

where  $\alpha$  is the fraction of  $H_2$ O that dissociates

 $\alpha$ =1 complete dissociation, no net heat released  $\alpha$ =0 no dissociation, max energy released

Can calculate the product mixture entropy as a function of  $\boldsymbol{\alpha}$ 

$$\overline{s} = \sum_{i=1}^{n} y_i \left( \overline{s}_i^o - R_i \ln y_i \right) - \overline{R} \ln(P/P_o)$$

# **Chemical Equilibrium**



The second Law of thermodynamics states that  $dS \ge 0$ 

Mixture spontaneously shifts towards maximum entropy

Condition for equilibrium is dS = 0

#### **Adiabatic Flame Temperature for Products at Equilibrium**

$$\begin{split} H_2 + 0.5(O_2 + 3.76N_2) &\rightarrow aH_2O + bN_2 + cO_2 + dH_2 \\ &+ eH + fO + gOH + hNO + jN + \cdots \end{split}$$

• One can calculate the AFT for the above stoichiometric reaction where the products are at equilibrium:  $\sum_{P} n_i \overline{h_i}(T_a) = \sum_{R} n_i \overline{h_i}(T_1)$ 

• Note dissociation in the products will result in a lower AFT since dissociation reactions are endothermic.

• Computer equilibrium programs are used for these calculations

#### **Chemical Kinetics**

Global (or overall) reactions describe the initial and final states:

 $H_2 + 0.5(O_2 + 3.76N_2) \rightarrow 1H_2O + 3.76N_2$ 

First and Second Laws of thermodynamics are used to predict the final equilibrium state of the products after the reaction is complete.

Chemical kinetics deals with how fast the reaction proceeds.

$$v_F F + v_A A \rightarrow v_C C + v_D D$$

How fast the fuel is consumed is of interest, the **reaction rate**  $\omega$ ''' is defined as: d[F]

$$\omega''' = -\frac{a[F]}{dt}$$
 [F] has units mol/cm<sup>3</sup>

The global hydrogen-oxygen reaction proceeds via the following elementary reactions, collectively known as a **reaction mechanism**:

$H_2 + M \rightarrow H + H + M$	}	- Chain initiation	
$H + O_{2} + M \rightarrow HO_{2} + M$ $HO_{2} + H_{2} \rightarrow H_{2}O + OH$ $OH + H_{2} \rightarrow H_{2}O + H$		Chain propagation	
$H + O_2 \rightarrow OH + O$ $H_2 + O \rightarrow OH + H$	}	Chain branching	
$H + OH + M \rightarrow H_2O + M$ $H + H + M \rightarrow H_2 + M$ $O + O + M \rightarrow O_2 + M$	}	Chain termination	

(M is any species present that acts as a collision partner)

#### **Reaction Rate**

Consider the elementary reaction

 $H + O_2 \rightarrow O + OH$ 

Kinetic theory of gases gives the following expression for the reaction rate:



$$(\sigma_{\rm H} + \sigma_{\rm O2})/2$$

$$-\frac{d[H]}{dt} = k[H][O_2]$$

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#### **Reaction Rate, cont'd**

Most common form is the Arrhenius form:

$$k = AT^{b} \exp\left(-\frac{E_{a}}{\overline{R}T}\right)$$

where A and b are the rate coefficients,  $E_a$  is the activation energy and  $\overline{R}$  is the universal gas constant. so

The values of A, b and  $E_a$  are tabulated for different reactions.

#### **Rate Coefficients for H2-O2 Reactions**

Reactions	<i>A</i> ((cm³/gmol) <sup>n-1</sup> /	<i>A b</i> ((cm³/gmol) <sup>ո-1</sup> /s)*		Temperature range (K)	
$H + O_2 \rightarrow OH + O$	1.2 - 1017	-0.91	69.1	300-2,500	
$OH + O \rightarrow O_2 + H$	1.8 - 1013	. 0	0	300-2,500	
$O + H_2 \rightarrow OH + H$	1.5 - 107	2.0	31.6	300-2,500	
$OH + H_2 \rightarrow H_2O + H$	1.5 - 108	1.6	13.8	300-2,500	
$H + H_2O \rightarrow OH + H_2$	4.6 - 108	1.6	77.7	300-2,500	
$Q_1 + H_2O \rightarrow OH + OH$	1.5 - 1010	1.14	72.2	300-2,500	
$H + H + M \rightarrow H_2 + M$					
$M \cong A_F(low P)$	6.4 . 1017	-1.0	0	300-5.000	
$\mathbf{M}=H_2 \ (\mathrm{low} \ P)$	0.7 - 1016	-0.6	0	100-5,000	
$H_2 + M \rightarrow H + H + M$	•	20			
M = Ar (low P)	2.2 - 1014	0	402	2,500-8,000	
$\mathbf{M} = \mathbf{H}_2 \ (\mathbf{low} \ \mathbf{P})$	8.8 - 1014	0	402	2,500-8,000	
$H + OH + M \rightarrow H_2O + M$			20		
$M = H_2O \ (low P)$	1.4 - 1023	-2.0	0	1,000-3,000	
$H_2O + M \rightarrow H + OH + M$					
$M = H_2O (low P)$	1.6 - 1017	0	478	2,000-5,000 🛇	
$0 + 0 + M \rightarrow O_2 + M$			1		
$\mathbf{M} = \mathbf{Ar} \ (\mathbf{low} \ \mathbf{P})$	1.0 - 1017	-1.0	0	300-5,000	
$O_2 + M \rightarrow O + O + M$				•	
M = Ar (low P)	1.2 - 1014	0	451	2.000-10.000	

\* *n* is the reaction order

#### **Reaction Rate for Global Reaction**

Even for the simplest hydrocarbon fuels the chemistry is very complicated. The GRI HC mechanism has 49 species and 227 elementary reactions.

For engineering purposes easier to use global description of reaction:

$$v_f(Fuel) + v_{O_2}O_2 + v_i(Inert) \rightarrow v_p(product)$$

Empirical correlations have been developed for the fuel reaction rate:

$$\frac{d[Fuel]}{dt} = -A \exp\left(-\frac{E}{\overline{R}T}\right) \cdot [Fuel]^n [O_2]^m [Inert]^l$$

where [] in units of gmol/cm<sup>3</sup>  $\overline{R}$  = 1.987 cal/gmolK *E* typically 20 - 40 kcal/gmol

Note this is a correlation so *n*, *m* and *l* don't have to be integers, typically l=0

# **Explosion Limits**

Perform an experiment where a fuel-oxygen mixture is injected into a preheated evacuated vessel and monitor the vessel pressure.



For a given fuel-oxygen mixture, e.g. stoichiometric, and fill pressure, if you vary the temperature of vessel you will find that there is a critical temperature above which an **explosion** occurs and below which an explosion does not occur (note there is no spark ignition).

An explosion is characterized by a rapid rise in vessel pressure faster than the normal pressure rise due to gas filling.

This critical temperature is referred to as the **autoignition** or **explosion limit temperature** 31

# **Explosion Limits**

If you repeat the experiment for different fill pressures and plot all the results on a pressure-temperature graph one can define an explosion limit curve.

For  $H_2$ - $O_2$  the shape of this limit curve can be explained by the temperature and pressure dependencies of the elementary reactions.



#### Hydrogen-oxygen reaction

Consider the following reaction mechanism subset:

$$H_2 + M \to 2H + M \tag{1}^*$$

- $H + O_2 \to O + OH \tag{2}$
- $O + H_2 \to H + OH \tag{3}$
- $OH + H_2 \rightarrow H_2O + H$  (4)
- $O + H_2 O \rightarrow OH + OH$  (5)

\*Dissociation energy of  $H_2$  less than  $O_2$  so initiation involves producing H

Reverse reactions for (2), (3), (5) not important since  $[R] \ll [H_2]$ 

Once *H* generated there is no chain reaction barrier to scavenge *H* and prevent explosion (recombination reactions are slow because 3 body)

Can mitigate explosion by adding molecules that scavenges *H* 

# Hydrogen-oxygen explosion Limits

# First Limit:

At low pressure wall collisions are important, free radicals are lost so chain termination step. This step overrides reaction (2) at very low P

# **Second Limit:**

At higher pressure 3<sup>rd</sup> order reactions become important because higher collision frequency

 $H + O_2 + M \rightarrow HO_2 + M$ 

Hydroperoxy radical is relatively nonreactive, diffuses to wall and destroyed, so the reaction scavenges *H* slowing the reaction

#### Third Limit:

The following chain branching reactions overtake the stabilizing  $HO_2$ 

$$HO_2 + H_2 \rightarrow H_2O_2 + H$$
$$H_2O_2 + M \rightarrow 2OH + M$$

and overall reaction becomes explosive again

#### **Constant Volume Explosion**

Homogeneous reaction (no flame) in a constant volume adiabatic bomb

First Law:  $\frac{du}{dt} = c_v \frac{dT}{dt} = -\frac{dC_F}{dt}Q$ 

where Q is the energy released per unit mole of fuel

$$c_{v}dT = -QdC_{F}$$

$$c_{v}\int_{T(t)}^{T_{MAX}} dT = -Q\int_{C_{F}(t)}^{0} dC_{F}$$

$$C_{F}(t) = \frac{c_{v}}{Q} \left(T_{MAX} - T(t)\right)$$

At 
$$t=0 \rightarrow T=T_o$$
,  $C_F=C_{F_o}$   $C_F(t) = C_{F_o} \left( \frac{T_{MAX} - T(t)}{T_{MAX} - T_o} \right)$ 

Consider a reaction rate of the form:

$$\frac{dC_F}{dt} = -K_o C_F^n e^{-E_a/RT}$$

$$\frac{dT}{dt} = -\frac{Q}{c_v} \frac{dC_F}{dt} = \frac{QK_o}{c_v} \left(\frac{c_v}{Q} (T_{MAX} - T)\right)^n e^{\frac{-E_a}{RT}}$$

Without any loss of generality, take n=1, and define  $t^* = K_o t$ 

$$\frac{dT}{dt^*} = (T_{MAX} - T)e^{-E_a/RT}$$

Also, 
$$\frac{dC_F}{dt} = -K_o C_F e^{\frac{-E_a}{RT}} = -K_o \left\{ C_{F_o} \left( \frac{T_{MAX} - T}{T_{MAX} - T_o} \right) \right\} e^{\frac{-E_a}{RT}}$$

Defining  $C_F^* = C_F / C_{F_o}$ 

$$\frac{dC_F^*}{dt^*} = -\left(\frac{T_{MAX} - T}{T_{MAX} - T_o}\right)e^{-E_a/RT}$$



#### **Laminar Premixed Flames**

In an explosion the flame propagates relative to a fixed observer



For a given P, T,  $\phi$  a flame has two basic properties:

- a) adiabatic flame temperature,  $T_{ad}$
- b) laminar burning velocity,  $S_l$

Note,  $S_l$  is defined in terms of the approaching unburned gas velocity and is subsonic

#### **Pressure Drop Across a Laminar Flame**

From conservation of mass and momentum

$$P_u - P_b = \left(\rho_u S_l\right)^2 \left[\frac{1}{\rho_b} - \frac{1}{\rho_u}\right]$$

Using typical values:  $S_l \approx 0.5 \text{ m/s}$   $\rho_u \approx 1 \text{ kg/m}^3$  $\rho_b \approx \rho_u (T_u/T_b) = I(300/2300)$ 

$$P_{u} - P_{b} = \left(\frac{1kg}{m^{3}} \cdot 0.5m/s\right)^{2} \left[\frac{2300}{300} - \frac{1}{1}\right] = 1.7 \frac{kg}{m \cdot s^{2}}$$

Typically 
$$P_u = 1$$
 atm  $= 10^5$  kg/m-s<sup>2</sup>  $\rightarrow P_u \approx P_b$ 

#### **Combustion Wave Analysis**

Steady-state combustion occurs within the control volume and equilibrium is achieved at state 2

$$P_2, \rho_2, T_2 \checkmark u_2 \checkmark u_1 P_1, \rho_1, T_1$$

 $u_1$  is the wave velocity

$$\rho_1 u_1 = \rho_2 u_2$$

$$P_2 - P_1 = \rho_1 u_1 (u_1 - u_2)$$

$$\frac{u_1^2}{2} + h_1 = \frac{u_2^2}{2} + h_2$$

For perfect gas

$$P = \rho RT$$
 and  $h = h_f^o + c_p (T - T^o)$  where  $T^o = 0K$ 

**Energy** equation

$$\frac{u_{1}^{2}}{2} + c_{p_{1}}T_{1} + q = \frac{u_{2}^{2}}{2} + c_{p_{2}}T_{2} \quad \text{where } q = h_{f_{1}}^{o} + h_{f_{2}}^{o} \text{ chemical energy per unit mass}$$

Have 5 unkowns ( $P_2$ , $\rho_2$ , $T_2$ ,  $u_2$ ,  $u_1$ ) and only 4 equations

Combining conservation of mass and momentum yields the Rayleigh eqn

$$\frac{P_2}{P_1} = -\left(\frac{\rho_1 u_1^2}{P_1}\right)\frac{\rho_1}{\rho_2} + \left(1 + \frac{\rho_1 u_1^2}{P_1}\right)$$

Combining conservation of momentum and energy yields the Hugoniot eqn

$$c_{p}T_{2} - (c_{p}T_{1} + q) = \frac{1}{2}(P_{2} - P_{1})\left(\frac{1}{\rho_{1}} + \frac{1}{\rho_{2}}\right)$$

$$\times \frac{\rho_{1}}{P_{1}} \qquad \left(\frac{k_{2}}{k_{2} - 1}\right)\frac{P_{2}}{\rho_{2}} - \left(\frac{k_{1}}{k_{1} - 1}\right)\frac{P_{1}}{\rho_{1}} - q = \frac{1}{2}(P_{2} - P_{1})\left(\frac{1}{\rho_{1}} + \frac{1}{\rho_{2}}\right)$$

If it is assumed that there is no change in the specific heat  $(k_1 = k_2 = k)$ :

$$\left(\frac{k}{k-1}\right)\left[\left(\frac{\rho_{1}}{\rho_{2}}\right)\left(\frac{P_{2}}{P_{1}}\right)-1\right]-\frac{\rho_{1}q}{P_{1}}=\frac{1}{2}\left(\frac{P_{2}}{P_{1}}-1\right)\left(1+\frac{\rho_{1}}{\rho_{2}}\right)$$

where  $\frac{\rho_1 q}{P_1} = \frac{(k-1)q}{c_v T_1} = \frac{\text{chemical energy released}}{\text{initial sensible energy content}}$ 

### **Hugoniot Curves for Combustion Waves**



The Hugoniot equation gives all possible end states for given heat release q including the constant volume and pressure process end states 42

#### **Entropy Change Across Combustion Wave**



Second Law requires that  $s_2 - s_1 \ge 0$ ,

For q > 0 can have expansive and compressive combustion waves

 $P_2/P_1 < 1$ ,  $\rho_1/\rho_2 > 1$  deflagration waves

 $P_2/P_1 > 1$ ,  $\rho_1/\rho_2 < 1$  detonation waves

### Laminar Flame Propagation and Structure

Successive ignition of layers of unburned gas mixture ahead of the flame front due to the diffusion of heat and mass from the combustion products

#### Flame structure:

Preheat zone:

No chemical reactions, temperature rise due to thermal diff.

Reaction zone:

Fast chemistry – bimolecular reactions where reactants are consumed and intermediates such as radicals are formed

Slow chemistry – three-body radical recombination reactions where products are formed

Gradients in temperature and radicals in the fast chemistry region are the driving force for flame propagation  $\rightarrow$  a laminar flame is diffusion wave

#### **Flame Structure**



#### **Maillard-LeChatelier Flame Theory**

Define a fictitious ignition temperature  $T_i$  below which no chemical reactions

Energy balance (steady-state) of preheat zone:



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#### **Maillard-LeChatelier Flame Theory**

Species continuity (assuming reactants are completely consumed):

 $\rho_u S_l A = \overline{w'''} A \delta$   $\overline{w'''}$  average reaction rate (units:  $kg/m^3-s$ )

$$\overline{w'''} = \overline{\rho_F^a \rho_O^b A \exp\left(-\frac{E_a}{\overline{R}T}\right)} = \overline{\rho_F^{n-b} \rho_O^b k} \approx k\rho^n \approx kP^n$$

This gives  $\delta = \frac{\rho_u S_l}{w''}$ , substituting yields:  $S_l = \frac{\alpha}{\delta} = \frac{\alpha w''}{\rho_u S_l} = \frac{\alpha}{S_l (\rho_u / w'')} = \frac{\alpha}{S_l (t_{chem})}$ 

Flame velocity, 
$$S_l \approx \sqrt{\frac{\alpha}{t_{chem}}}$$

#### Laminar Flame as a Diffusion Wave

$$S_l \approx \sqrt{\frac{\alpha}{t_{chem}}} = \sqrt{\frac{10^{-5} m^2 / s}{10^{-3} s}} = 10^{-1} m / s$$

Measured values for stoichiometric HC-air mixtures  $\approx 0.3 - 0.5$  m/s

Flame velocity is proportional to diffusivity and inversely proportional to the combustion time  $(1/T_{ad})$  so higher  $s_l$  for hydrogen-air mixtures ~1.5 m/s

The flame thickness can be approximated by:

$$\delta \approx \sqrt{\alpha t_{chem}} = \sqrt{10^{-5} m^2 / s \cdot 10^{-3} s} = 10^{-4} m$$

#### Laminar Burning Velocity Data



#### **Experimental Hydrogen-air Laminar Burning Velocity**



A.E. Dahoe, Laminar burning velocities of hydrogen–air mixtures from closed vessel gas explosions, Journal of Loss Prevention in the Process Industries 18 (2005) 152–166



#### Effect of flame stretch on S<sub>L</sub>

Flame stretch due to flame curvature effects the burning velocity



Karlovitz proposed that the stretched burning velocity is  $S = S_L - Ma \delta \alpha$ 

where Ma is the Markstein number and flame stretch rate  $\alpha = (1/A_F)(dA_F/dt)$ 

Stretch reduces the burning velocity, only important for small flame radius

Stretch also occurs due to in homogeneities in the upstream flow (flow strain):

- flow expansion results in S>S<sub>L</sub>
- flow compression results in  $S{<}S_{\rm L}$

### **Minimum Flame Kernal Size**

Consider a 1-D problem where energy is added to a slab of mixture to raise its temperature to  $T^*$ 

The heat release rate is insufficient to maintain the temperature, diffusion of heat out of the slab causes the centre temperature to drop



Want to find the minimum value of  $d_T$  when the peak temperature equals  $T_{ad}$  that results in a flame propagating away from the slab

Energy balance:

$$\rho c_p(d_T A) \frac{dT}{dt} = (d_T A) w''' q - 2kA \left(\frac{T_{ad} - T_o}{d_T / 2}\right)$$

Heat production Heat loss

The critical condition is when the heat production equals heat loss

$$(d_T A)w'''q = 2kA\left(\frac{T_{ad} - T_o}{d_T/2}\right)$$
$$d_T^2 = \frac{4k(T_{ad} - T_o)}{w'''q} \qquad \qquad \alpha = \frac{k}{\rho c_p}$$
$$= 2\sqrt{\frac{\alpha\rho c_p(T_{ad} - T_o)}{w'''q}}$$

But  $q = c_p(T_{ad} - T_o)$  chemical energy required to raise temperature to  $T_{ad}$ 

$$\begin{aligned} d_T &= 2\sqrt{\frac{\alpha\rho}{w'''}}\\ \text{Recall} \quad S_l^2 &= \frac{\alpha w'''}{\rho_u} \to \alpha = \frac{\rho_u S_l^2}{w'''}\\ d_T &= 2\sqrt{\frac{\alpha\rho}{w'''}} = 2\sqrt{\frac{\rho^2 S_l^2}{(w''')^2}} = 2\delta \quad \text{ for a sphere get } d_T = \sqrt{6}\delta \end{aligned}$$

Minimum kernel size is on the order of the laminar flame thickness <sup>54</sup>

#### **Minimum Ignition Energy**

Assume the energy added by the spark heats up the minimum kernal size to the adiabatic flame temperature

$$E_{ign} = \frac{4}{3}\pi \left(\frac{d_T}{2}\right)^3 \rho c_p (T_{ad} - T_1)$$
$$= \frac{4}{3}\pi \left(\frac{\sqrt{6\delta}}{2}\right)^3 \rho c_p (T_{ad} - T_1)$$
$$= 7.7\delta^3 \rho c_p (T_{ad} - T_1)$$

Effect of initial pressure:  $E_{ign} \propto P^{-3}P = P^{-2}$  lower pressure need more energy

Effect of initial temperature:  $E_{ign} \propto T_{ad} - T_1$  higher temperature less energy

#### **Quenching Diameter**

As a flame propagates through a pipe heat is lost from the flame to the wall



Critical condition: Rate of heat production = rate of heat loss

$$\frac{\pi d_q^2}{4} \delta w''' q = \pi d \delta k \left( \frac{T_{ad} - T_1}{d/2} \right)$$
$$d_q^2 = \frac{8k(T_{ad} - T_1)}{w'''q}$$
$$= 2d_T^2 = 8\delta^2$$
$$d_q = \sqrt{6}\delta = \sqrt{6}\alpha / S_l$$
Number (Pe)
$$Pe = \frac{d_q S_l}{\alpha} = 2.4$$

Principle behind coal miner's lamp

Peclet

# **Flammability Limits**

A flame will only propagate in a fuel-air mixture within a composition range known as the **flammability limits**.

The fuel-lean limit is known as the **lower flammability limit** and the fuel-rich limit is known as the **upper flammability limit**.

The flammability limit is affected by both the mixture initial pressure and temperature.

	3	Flammability Limits		Quenching Distance		Minimum Ignition Energy	
Fuel	<b>₽<sub>nie</sub> (Lean or</b> Lower Limit)	∮ <sub>max</sub> (Rich or Upper Limit)	Stoichiometric Mass Air-Fuel Ratio	For + - 1 (mm)	Absolute Minimum (mm)	For $= 1$ (10 <sup>-5</sup> J)	Absolute Minimum (10 <sup>-5</sup> J)
Acetylene, C <sub>2</sub> H <sub>2</sub>	0.19 <sup>b</sup>	oo <sup>b</sup>	13.3	2.3	-	3	_
Carbon monoxide, CO	0.34	6.76	2.46		-	_	
n-Decane, C15H22	0.36	3.92	15.0	2.1°		-	-
Ethane, C2H4	0.50	2.72	16.0	2.3	1.8	42	24
Ethylene, C.H.	0.41	> 6.1	14.8	1.3		9.6	
Hydrogen, Hy	0.14 <sup>b</sup>	2.546	34.5	0.64	0.61	2.0	1.8
Methane, CH.	0.46	1.64	17.2	2.5	2.0	33	29
Methanol, CH <sub>1</sub> OH	0.48	4.08	6.46	1.8	1.5	21.5	34
n-Octane, CaH12	0.51	4.25	15.1				-
Propane, C <sub>3</sub> H <sub>8</sub>	0.51	2.83	15.6	2.0	1.8	30.5	26

#### Landau–Darrieus flame Instabilities

Flame instabilities cause laminar flames to wrinkle thereby increasing the flame area and volumetric burning rate



Streamlines in the burnt gas converge behind the convex part of the front and diverge behind the concave parts – accentuates initial winkles

Unstable at all wavelengths, only linear growth phase

#### Effect of thermal diffusion

Consider a wrinkled flame, diffusive fluxes of heat shown at cusps



For top portion of the flame heat flux lines diverge, so reactant temperature lower leading to lower burning velocity  $\rightarrow$  stabilizing

For bottom portion of the flame heat flux lines converge, so reactant temperature higher leading to higher burning velocity  $\rightarrow$  stabilizing

#### Effect of mass diffusion

Important if mixture components have very different diffusivity (e.g.,  $H_2$  compared to  $O_2$  and  $N_2$ , important for lean hydrogen-air mixtures)

Diffusive fluxes of limiting component shown at cusps



For top portion of the flame mass flux lines converge, so limiting component concentration increases leading to higher burning velocity  $\rightarrow$  destabilizing

For bottom portion of the flame mass flux lines converge, so limiting component concentration decreases leading to lower burning velocity  $\rightarrow$  destabilizing

#### **Effect of Lewis Number**

Lewis number defined as Le=  $\chi$  / D<sub>L</sub>

Thermal diffusivity,  $\chi$ , and molecular diffusivity of the limiting component, D<sub>L</sub>.

Le<1, mass dominates thermal diffusion, so wrinkles increase in amplitude

Le>1 opposite effect, a tendency for smoothing out flame wrinkles, which leads to stable flames.

#### Hydrogen flame instabilities

Since hydrogen is very light compared to air strong mass diffusion effects



10%H2 in air (Le=0.35)



70%H2 in air (Le= 3.8)

#### Flame Velocity

The laminar burning velocity is measured relative to the unburned gas ahead and the **flame velocity**  $V_f$  is measured relative to a fixed observer.

If the flame is propagating in a closed-ended tube the velocity measured is the flame velocity and can be up to 8 times the burning velocity.

This is because the density of the products is lower than that of reactants, so a flow is generated ahead of the flame

$$V_{b}=0 \qquad V_{f} \quad V_{u} \qquad V_{f} \quad V_{b}=V_{f} \qquad V_{f} - V_{u}=S_{l}$$

$$\rho_{b} \qquad \rho_{u} \qquad \rho_{b} \qquad \rho_{u}$$

$$\rho_u \cdot S_l \cdot A = \rho_b \cdot V_f \cdot A \rightarrow V_f = \left(\frac{\rho_u}{\rho_b}\right) \cdot S_l \approx 8S_l$$

$$V_f = \left(\frac{\rho_u}{\rho_b}\right) \cdot S_l = \left(\frac{\rho_u}{\rho_b}\right) \left(V_f - V_u\right) \rightarrow V_u = \left(1 - \frac{\rho_b}{\rho_u}\right) V_f \approx \frac{7}{8} V_f$$

# **Turbulent Flames**

Flows become unstable at sufficiently high Reynolds numbers (Re >100)

The turbulent energy is stored at the integral scale (l) and energy is dissipated at the Kolmogorov scale ( $\eta$ )



Flame propagating into a turbulent flow is highly distorted

#### **Premixed Turbulent Flame Structure - Borghi Diagram**



Damkohler Number 
$$(Da) = \frac{\tau_L}{\tau_{chem}} = \frac{l/u'}{\delta_L/S_L} = \left(\frac{l}{\delta_L}\right) \left(\frac{S_L}{u'}\right)$$

Karlovitz Number (*Ka*) = 
$$\frac{\tau_{chem}}{\tau_{\eta}} = \frac{\delta_L / S_L}{\eta / u'} = \left(\frac{\delta_L}{\eta}\right) \left(\frac{u'}{S_L}\right)$$

. .

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We are interested in the situation where the flame thickness is smaller than the largest scale of turbulence.  $\left\{\frac{\delta_L}{r} < 1\right\}$ 

# Wrinkled laminar flame regime: $S_L > u'$ : distortions are damped out by the propagation of the flame $\left\{\frac{u'}{S_L} < 1\right\}$ **Corrugated Laminar flame regime:** $S_L < u'$ : flame cannot smoothen the fluctuations $\left\{ \frac{u'}{S_L} > 1 \right\}$

#### Thick flame regime:

Smallest eddies are smaller then the flame thickness  $\eta < \delta_L (Da > 1)$ Larger eddies wrinkle flame and smaller eddies roughen and puncture flame

