

Thermodynamics, Flame Temperature and Equilibrium

CEFRC Combustion Summer School

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Course Overview

Part I: Fundamentals and Laminar Flames

- Introduction
- Fundamentals and mass balances of combustion systems
- **Thermodynamics, flame temperature, and equilibrium** 
 - **Thermodynamic quantities**
 - Flame temperature at complete conversion
 - Chemical equilibrium
- Governing equations
- Laminar premixed flames: Kinematics and Burning Velocity
- Laminar premixed flames: Flame structure
- Laminar diffusion flames

First law of thermodynamics - balance between different forms of energy

- Change of specific internal energy: du
specific work due to volumetric changes: $\delta w = -pdv$, $v=1/\rho$
specific heat transfer from the surroundings: δq
- Related quantities
specific enthalpy (general definition): $h = u + pv$
specific enthalpy for an ideal gas: $h = u + \frac{\mathcal{R}T}{W}$
- Energy balance: $du = \delta q + \delta w$

Multicomponent system

- Specific internal energy and specific enthalpy of mixtures

$$u = \sum_{i=1}^k Y_i u_i, \quad h = \sum_{i=1}^k Y_i h_i.$$

- Relation between internal energy and enthalpy of single species

$$h_i = u_i + \frac{\mathcal{R}T}{W_i}, \quad i = 1, 2, \dots, k$$

Multicomponent system

- Ideal gas
 - u and h only function of temperature

$$h_i = u_i(T) + \frac{\mathcal{R}T}{W_i}, \quad i = 1, 2, \dots, k$$

- If c_{pi} is specific heat capacity at constant pressure and $h_{i,\text{ref}}$ is reference enthalpy at reference temperature T_{ref} , temperature dependence of partial specific enthalpy is given by

$$h_i = h_{i,\text{ref}} + \int_{T_{\text{ref}}}^T c_{pi} dT, \quad i = 1, 2, \dots, k$$

- Reference temperature may be arbitrarily chosen, most frequently used:

$$T_{\text{ref}} = 0 \text{ K} \quad \text{or} \quad T_{\text{ref}} = 298.15 \text{ K}$$

Multicomponent system

- Partial molar enthalpy H_i is

$$H_i = W_i h_i, \quad i = 1, 2, \dots, k,$$

and its temperature dependence is

$$H_i = H_{i,\text{ref}} + \int_{T_{\text{ref}}}^T C_{pi} dT, \quad i = 1, 2, \dots, k,$$

where the molar heat capacity at constant pressure is

$$C_{pi} = W_i c_{pi}, \quad i = 1, 2, \dots, k.$$

- In a multicomponent system, the specific heat capacity at constant pressure of the mixture is

$$c_p = \int_{i=1}^k Y_i c_{pi}.$$

Determination of Caloric Properties

- Molar reference enthalpies of chemical species at reference temperature are listed in [tables](#)
- [Reference enthalpies](#) of H_2 , O_2 , N_2 and solid carbon C_s were chosen as [zero](#), because they represent the chemical elements
- Reference enthalpies of combustion products such as CO_2 and H_2O are typically negative

Determination of Caloric Properties

- Temperature dependence of molar enthalpy, molar entropy, and molar heat capacities may be calculated from polynomials

$$\frac{C_{p,i}}{\mathcal{R}} = a_1 + a_2 T/\text{K} + a_3 (T/\text{K})^2 + a_4 (T/\text{K})^3 + a_5 (T/\text{K})^4$$

$$\frac{H_i}{\mathcal{R}T} = a_1 + a_2 \frac{T/\text{K}}{2} + a_3 \frac{(T/\text{K})^2}{3} + a_4 \frac{(T/\text{K})^3}{4} + a_5 \frac{(T/\text{K})^4}{5} + \frac{a_6}{T/\text{K}}$$

$$\frac{S_i}{\mathcal{R}} = a_1 \ln(T/\text{K}) + a_2 T/\text{K} + a_3 \frac{(T/\text{K})^2}{2} + a_4 \frac{(T/\text{K})^3}{3} + a_5 \frac{(T/\text{K})^4}{4} + a_7 + \ln(p/p_0)$$

- Constants a_j for each species i are listed in tables


Determination of Caloric Properties

NASA Polynomials for two temperature ranges and standard pressure $p = 1 \text{ atm}$

H₂	temperature range:	$1000 < T < 5000$		
	$a_1 = +0.2991\text{E}+01$	$a_2 = +0.7000\text{E}-03$	$a_3 = -0.5634\text{E}-07$	$a_4 = -0.9232\text{E} - 11$
	$a_5 = +0.1583\text{E}-14$	$a_6 = -0.8350\text{E}+03$	$a_7 = -0.1355\text{E}+01$	
	temperature range:	$300 < T < 1000$		
O₂	temperature range:	$1000 < T < 5000$		
	$a_1 = +0.3698\text{E}+01$	$a_2 = +0.6135\text{E}-03$	$a_3 = -0.1259\text{E}-06$	$a_4 = +0.1775\text{E} - 10$
	$a_5 = -0.1136\text{E}-14$	$a_6 = -0.1234\text{E}+04$	$a_7 = +0.3189\text{E}+01$	
	temperature range:	$300 < T < 1000$		
N₂	temperature range:	$1000 < T < 5000$		
	$a_1 = +0.2927\text{E}+01$	$a_2 = +0.1488\text{E}-02$	$a_3 = -0.5685\text{E}-06$	$a_4 = +0.1010\text{E} - 09$
	$a_5 = -0.6753\text{E}-14$	$a_6 = -0.9228\text{E}+03$	$a_7 = +0.5981\text{E}+01$	
	temperature range:	$300 < T < 1000$		
N₂	temperature range:	$1000 < T < 5000$		
	$a_1 = +0.3299\text{E}+01$	$a_2 = +0.1408\text{E}-02$	$a_3 = -0.3963\text{E}-05$	$a_4 = +0.5642\text{E} - 08$
	$a_5 = -0.2445\text{E}-11$	$a_6 = -0.1021\text{E}+04$	$a_7 = +0.3950\text{E}+01$	
	temperature range:	$300 < T < 1000$		

Course Overview

Part I: Fundamentals and Laminar Flames

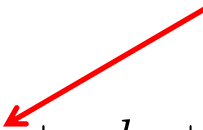
- Introduction
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- Chemical equilibrium

Flame Temperature at Complete Conversion

- First law of thermodynamics for an **adiabatic** system at **constant pressure** ($\delta q = 0, dp = 0$) with only reversible work ($\delta w = -pdv$)

- From first law $du = \delta q + \delta w = -pdv$

with $dh = du + pdv + vdp$



follows $dh = 0$

- Integrated from the unburnt (u), to burnt (b) gives

$$h_u = h_b$$

or

$$\sum_{i=1}^k Y_{i,u} h_{i,u} = \sum_{i=1}^k Y_{i,b} h_{i,b}$$

Flame Temperature at Complete Conversion

- With

$$\sum_{i=1}^k Y_{i,u} h_{i,u} = \sum_{i=1}^k Y_{i,b} h_{i,b}.$$

and

$$h_i = h_{i,\text{ref}} + \int_{T_{\text{ref}}}^T c_{pi} dT, \quad i = 1, 2, \dots, k$$

follows

$$\sum_{i=1}^k (Y_{i,u} - Y_{i,b}) h_{i,\text{ref}} = \int_{T_{\text{ref}}}^{T_b} c_{p,b} dT - \int_{T_{\text{ref}}}^{T_u} c_{p,u} dT.$$

- Specific heats to be calculated with the mass fractions of the burnt and unburnt gases

$$c_{p,b} = \sum_{i=1}^k Y_{i,b} c_{pi}(T), \quad c_{p,u} = \sum_{i=1}^k Y_{i,u} c_{pi}(T).$$

Flame Temperature at Complete Conversion

- For a one-step global reaction, the **left hand side** of

$$\underline{\sum_{i=1}^k (Y_{i,u} - Y_{i,b}) h_{i,\text{ref}}} = \int_{T_{\text{ref}}}^{T_b} c_{p,b} dT - \int_{T_{\text{ref}}}^{T_u} c_{p,u} dT$$

may be calculated by integrating $\frac{dY_i}{\nu_i W_i} = \frac{dY_1}{\nu_1 W_1}, \quad i = 2, \dots, k$

which gives $Y_{i,u} - Y_{i,b} = (Y_{F,u} - Y_{F,b}) \frac{\nu_i W_i}{\nu_F W_F}, \quad i = 1, 2, \dots, k,$

/ h_{i,ref}*

and finally $\underline{\sum_{i=1}^k (Y_{i,u} - Y_{i,b}) h_{i,\text{ref}}} = \frac{(Y_{F,u} - Y_{F,b})}{\nu_F W_F} \sum_{i=1}^k \nu_i W_i h_{i,\text{ref}}.$

Flame Temperature at Complete Conversion

- Definition: **Heat of combustion**

$$Q = - \sum_{i=1}^k \nu_i W_i h_i = - \sum_{i=1}^k \nu_i H_i$$

- Heat of combustion changes very little with temperature

- Often set to:

$$Q_{\text{ref}} = - \sum_{i=1}^k \nu_i H_{i,\text{ref}}$$

- **Simplification:** $T_u = T_{\text{ref}}$ and assume $c_{p,b}$ approximately constant
 - For combustion in air, nitrogen is dominant in calculating $c_{p,b}$
 - Value of $c_{p,i}$ somewhat larger for CO_2 , somewhat smaller for O_2 , while that for H_2O is twice as large
- Approximation for specific heat of burnt gas for **lean and stoichiometric mixtures** $c_p = 1.40 \text{ kJ/kg/K}$

Flame Temperature at Complete Conversion

$$\frac{(Y_{F,u} - Y_{F,b})}{\nu_F W_F} \sum_{i=1}^k \nu_i W_i h_{i,\text{ref}} = \int_{T_{\text{ref}}}^{T_b} c_{p,b} dT - \int_{T_{\text{ref}}}^{T_u} c_{p,u} dT$$

- Assuming c_p constant and $Q = Q_{\text{ref}}$, the **flame temperature at complete conversion for a lean mixture** ($Y_{F,b} = 0$) is calculated from

$$\frac{(Y_{F,u} - Y_{F,b})}{\nu_F W_F} \sum_{i=1}^k \nu_i W_i h_{i,\text{ref}} = c_p (T_b - T_u)$$

→ Coupling function between fuel mass fraction and temperature!

- With $\nu_F = -\nu'_F$ follows

$$T_b - T_u = \frac{Q_{\text{ref}} Y_{F,u}}{c_p \nu'_F W_F}$$

Flame Temperature at Complete Conversion

- For a rich mixture

$$Y_{i,u} - Y_{i,b} = (Y_{F,u} - Y_{F,b}) \frac{\nu_i W_i}{\nu_F W_F}, \quad i = 1, 2, \dots, k,$$

should be replaced by

$$Y_{i,u} - Y_{i,b} = (Y_{O_2,u} - Y_{O_2,b}) \frac{\nu_i W_i}{\nu_{O_2} W_{O_2}}, \quad i = 1, 2, \dots, k$$

- One obtains similarly for complete consumption of the oxygen ($Y_{O_2,b} = 0$)

$$T_b - T_u = \frac{Q_{\text{ref}} Y_{O_2,u}}{c_p \nu'_{O_2} W_{O_2}}$$

Flame Temperature at Complete Conversion

- Equations $T_b - T_u = \frac{Q_{\text{ref}} Y_{F,u}}{c_p \nu'_F W_F}$ and $T_b - T_u = \frac{Q_{\text{ref}} Y_{O_2,u}}{c_p \nu'_{O_2} W_{O_2}}$

may be expressed in terms of the [mixture fraction](#)

- Introducing $Y_{F,u} = Y_{F,1} Z$ and $Y_{O_2,u} = Y_{O_2,2}(1 - Z)$

and specifying the temperature of the unburnt mixture by

$$T_u(Z) = T_2 - Z(T_2 - T_1),$$

where

- T_2 is the temperature of the oxidizer stream and T_1 that of the fuel stream
- c_p assumed to be constant

Flame Temperature at Complete Conversion

- Equations $T_b - T_u = \frac{Q_{\text{ref}} Y_{F,u}}{c_p \nu'_F W_F}$ and $T_b - T_u = \frac{Q_{\text{ref}} Y_{O_2,u}}{c_p \nu'_{O_2} W_{O_2}}$

then take the form

$$T_b(Z) = T_u(Z) + \frac{Q_{\text{ref}} Y_{F,1}}{c_p \nu'_F W_F} Z, \quad Z \leq Z_{st},$$

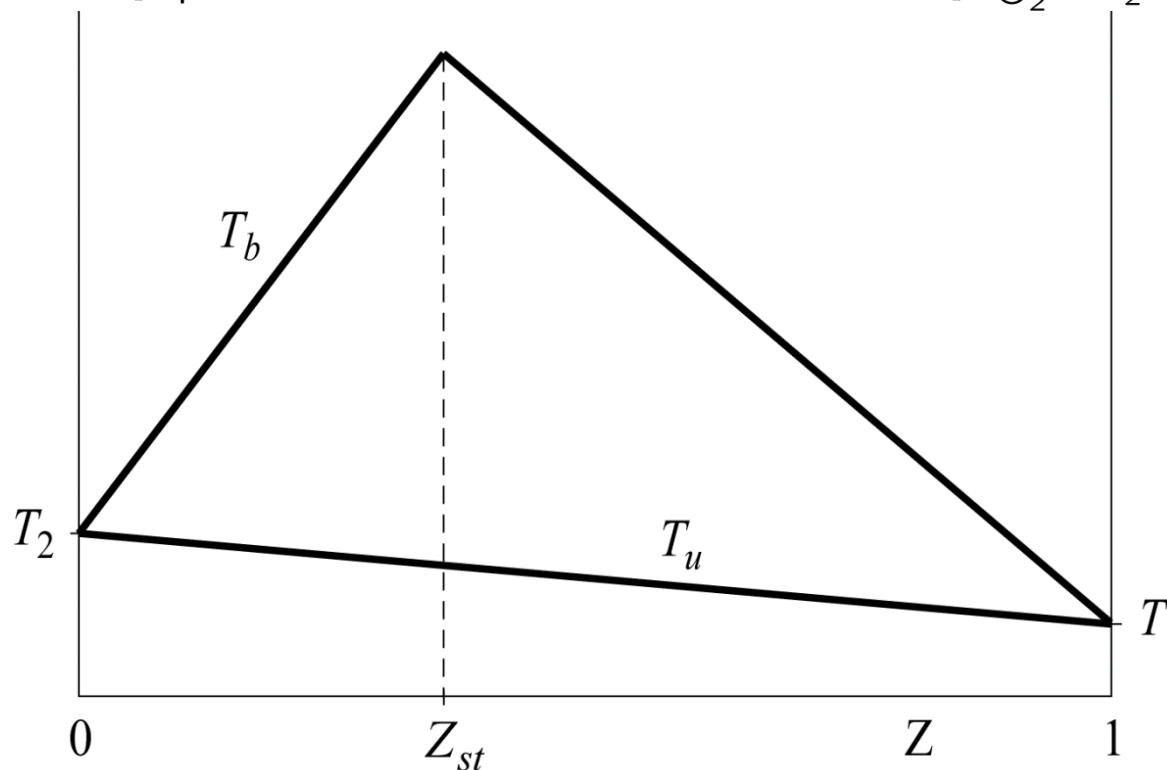
$$T_b(Z) = T_u(Z) + \frac{Q_{\text{ref}} Y_{O_2,2}}{c_p \nu'_{O_2} W_{O_2}} (1 - Z) \quad Z \geq Z_{st}$$

- The **maximum temperature** appears at $Z = Z_{st}$:

$$T_{st} = T_u(Z_{st}) + \frac{Y_{F,1} Z_{st} Q_{\text{ref}}}{c_p \nu'_F W_F} = T_u(Z_{st}) + \frac{Y_{O_2,2} (1 - Z_{st}) Q_{\text{ref}}}{c_p \nu'_{O_2} W_{O_2}}$$

Flame Temperature at Complete Conversion

$$T_b(Z) = T_u(Z) + \frac{Q_{\text{ref}} Y_{F,1}}{c_p \nu'_F W_F} Z, \quad Z \leq Z_{st}, \quad T_b(Z) = T_u(Z) + \frac{Q_{\text{ref}} Y_{O_2,2}}{c_p \nu'_{O_2} W_{O_2}} (1-Z) \quad Z \geq Z_{st}$$



Burke-Schumann Solution:



Infinitely fast, irreversible chemistry

Flame Temperature at Complete Conversion

- The table shows for combustion of pure fuels ($Y_{F,1} = 1$) in air ($Y_{O_2,2} = 0.232$) with $T_{u,st} = 300$ K and $c_p = 1.4$ kJ/kg/K

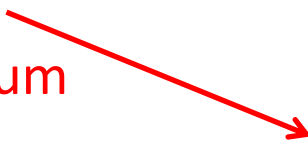
- stoichiometric mixture fraction
- stoichiometric flame temperatures

for some hydrocarbon-air mixtures

Fuel	Z_{st}	T_{st} [K]
CH ₄	0.05496	2263.3
C ₂ H ₆	0.05864	2288.8
C ₂ H ₄	0.06349	2438.5
C ₂ H ₄	0.07021	2686.7
C ₃ H ₈	0.06010	2289.7

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 - **Chemical equilibrium**
- 

- Assumption of **complete combustion** is approximation, because it disregards the possibility of dissociation of combustion products
- More general formulation is assumption of **chemical equilibrium**
 - Complete combustion then represents limit of infinitely large equilibrium constant (see below)
- Chemical equilibrium and complete combustion are valid in the limit of **infinitely fast reaction** rates only, which is often invalid in combustion systems



Importance of kinetics!

- Chemical equilibrium assumption
 - Only good for **hydrogen diffusion flames**
 - For **hydrocarbon** diffusion flames
 - Overpredicts formation of intermediates such as CO and H₂ for **rich conditions** by large amounts
- Equilibrium assumption represents an exact thermodynamic limit

- Partial molar **entropy** S_i of chemical species in a mixture of ideal gases depends on **partial pressure**

$$S_i = S_i^0 - \mathcal{R} \ln \frac{p_i}{p_0}, \quad i = 1, 2, \dots, k,$$

where $p_0 = 1 \text{ atm}$ and

$$S_i^0 = S_{i,\text{ref}}^0 + \int_{T_{\text{ref}}}^T \frac{C_{p_i}}{T} dT, \quad i = 1, 2, \dots, k$$

depends only on temperature

- Values for the reference entropy $S_{i,\text{ref}}$ are listed in tables

Chemical potential and the law of mass action

- Partial molar entropy may be used to define **chemical potential**

$$\mu_i = H_i - TS_i = \mu_i^0 + \mathcal{R}T \ln \frac{p_i}{p_0}, \quad i = 1, 2, \dots, k,$$

where

$$\mu_i^0 = H_{i,\text{ref}} - TS_{i,\text{ref}} + \int_{T_{\text{ref}}}^T C_{p_i} dT - T \int_{T_{\text{ref}}}^T \frac{C_{p_i}}{T} dT, \quad i = 1, 2, \dots, k$$

is chemical potential at 1 atm

- Condition for chemical equilibrium for l^{th} reaction is given by

$$\sum_{i=1}^k \nu_{il} \mu_i = 0, \quad l = 1, 2, \dots, r.$$

Chemical potential and the law of mass action

- Using
$$\mu_i = H_i - TS_i = \mu_i^0 + \mathcal{R}T \ln \frac{p_i}{p_0}, \quad i = 1, 2, \dots, k,$$

in
$$\sum_{i=1}^k \nu_{il} \mu_i = 0, \quad l = 1, 2, \dots, r.$$

leads to

$$-\sum_{i=1}^k \nu_{il} \mu_i^0 = \mathcal{R}T \ln \prod_{i=1}^k \left(\frac{p_i}{p_0} \right)^{\nu_{il}}, \quad l = 1, 2, \dots, r.$$

- Defining the equilibrium constant K_{pl} by

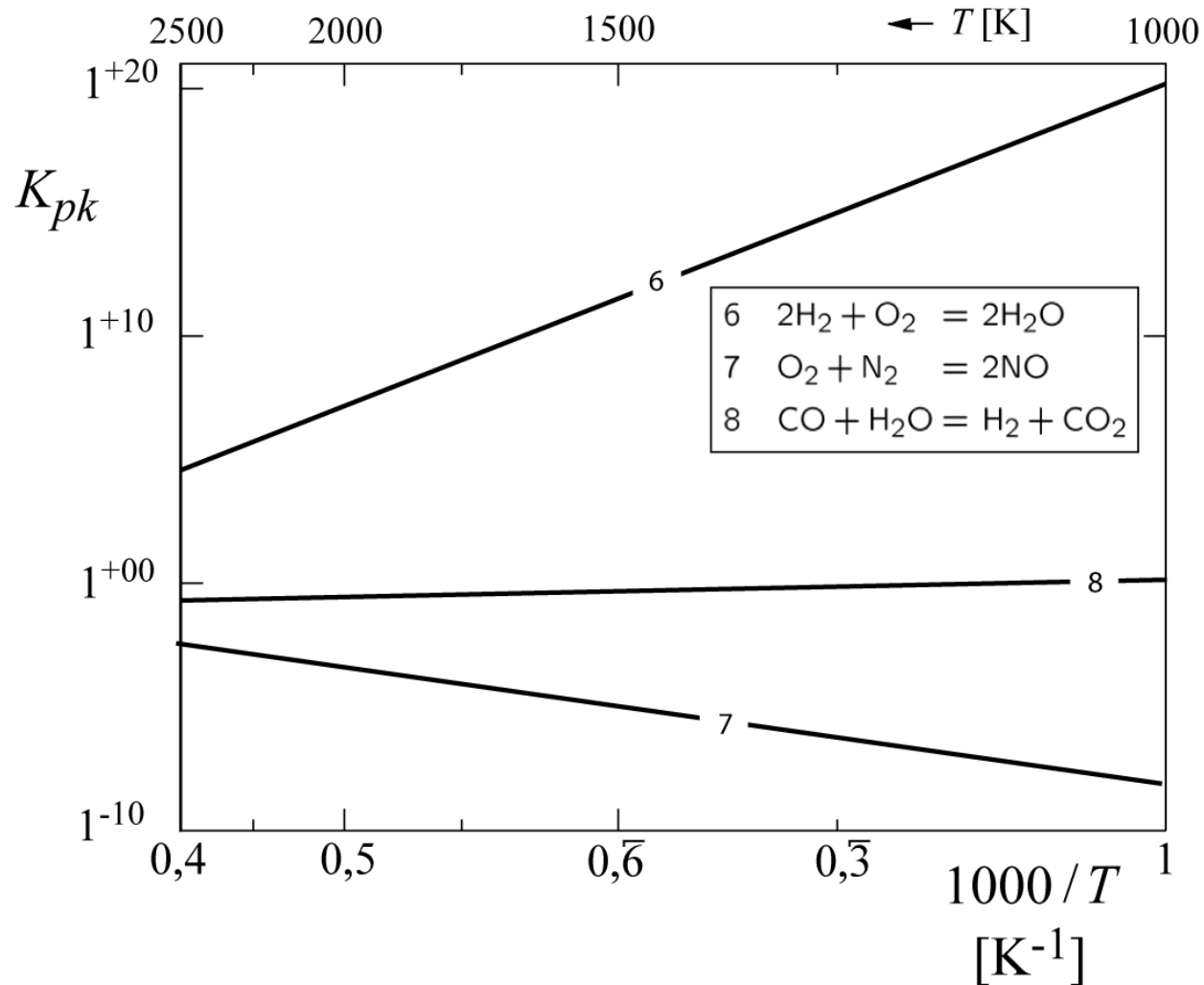
$$\mathcal{R}T \ln K_{pl} = -\sum_{i=1}^k \nu_{il} \mu_i^0, \quad l = 1, 2, \dots, r$$

one obtains the **law of mass action**

$$\prod_{i=1}^k \left(\frac{p_i}{p_0} \right)^{\nu_{il}} = K_{pl}(T), \quad l = 1, 2, \dots, r.$$

Chemical potential and the law of mass action

- Equilibrium constants for three reactions



Equilibrium Constants

- Calculation of equilibrium constants $K_{pk}(T)$ from the chemical potentials
 - with:
 - Enthalpies of formation
 - Entropies of formation
 - Heat capacities
- **Approximation**
 - Neglect temperature dependence of heat capacities

Approximation for Equilibrium Constants

- Equilibrium constants:
$$K_p(T) = \exp\left(\frac{-\sum_{i=1}^n \nu_i \mu_i^0}{\mathcal{R}T}\right)$$

- With
$$\frac{\mu_i^0}{\mathcal{R}T} = \frac{h_{i,m,\text{ref}}}{\mathcal{R}T} - \frac{s_{\text{ref}}}{\mathcal{R}} + \frac{1}{\mathcal{R}T} \int c_{p,i} dT + \int \frac{c_p}{\mathcal{R}T} dT$$

it follows for constant $c_{p,i}$

$$K_p(T) = \exp\left(\frac{-\sum_{i=1}^n \nu_i h_{i,m,\text{ref}}}{\mathcal{R}T}\right) \underbrace{\exp\left(\sum_{i=1}^n \nu_i s_{\text{ref}}/\mathcal{R}\right)}_{\text{const}} \underbrace{\exp\left(\sum_{i=1}^n \nu_i c_{p,i} \frac{T - T_{\text{ref}}}{\mathcal{R}T}\right)}_{\approx \text{const}} \underbrace{\exp\left(\sum_{i=1}^n \nu_i \frac{c_{p,i}}{\mathcal{R}} \ln \frac{T}{T_{\text{ref}}}\right)}_{\approx \exp(n \ln T)}$$

- Approximation:

$$K_p(T) = \exp\left(\frac{-\Delta h_{m,\text{ref}}}{\mathcal{R}T}\right) \underbrace{\exp\left(\sum_{i=1}^n \nu_i \pi_{i,A}\right)}_B \underbrace{\exp\left(\sum_{i=1}^n \nu_i \pi_{i,B} \ln T\right)}_{T^n}$$

Approximation for equilibrium constants

- With

$$B_p = \exp \left(\sum_{i=1}^n \nu_i \pi_{i,A} \right)$$

$$n_p = \sum_{i=1}^n \nu_i \pi_{i,B}$$

$$\Delta h_{m,\text{ref}} = \sum_{i=1}^n \nu_i h_{i,m,\text{ref}}$$

follows

$$K_p = B_p T^{n_p} \exp \left(\frac{-\Delta h_{m,\text{ref}}}{RT} \right)$$

Properties for gases at $T_{ref} = 298,15 \text{ K}$

		M_i [kg/kmol]	$h_{i,m,ref}$ [kJ/mol]	$S_{i,m,ref}$ [kJ/mol K]	$\pi_{A,i}$	$\pi_{B,i}$
1	H	1,008	217,986	114,470	-1,2261	1,9977
2	HNO	31,016	99,579	220,438	-1,0110	4,3160
3	OH	17,008	39,463	183,367	3,3965	2,9596
4	HO ₂	33,008	20,920	227,358	-,1510	4,3160
5	H ₂	2,016	0,000	130,423	-2,4889	2,8856
6	H ₂ O	18,016	-241,826	188,493	-1,6437	3,8228
7	H ₂ O ₂	34,016	-136,105	233,178	-8,4782	5,7218
8	N	14,008	472,645	153,054	5,8661	1,9977
9	NO	30,008	90,290	210,442	5,3476	3,1569
10	NO ₂	46,008	33,095	239,785	-1,1988	4,7106
11	N ₂	28,016	0,000	191,300	3,6670	3,0582
12	N ₂ O	44,016	82,048	219,777	-5,3523	4,9819

Properties for gases at $T_{ref} = 298,15 \text{ K}$

		M_i [kg/kmol]	$h_{i,m,ref}$ [kJ/mol]	$S_{i,m,ref}$ [kJ/mol K]	$\pi_{A,i}$	$\pi_{B,i}$
13	O	16,000	249,194	160,728	6,85561	1,9977
14	O ₂	32,000	0,000	204,848	4,1730	3,2309
15	O ₃	48,000	142,674	238,216	-3,3620	5,0313
16	NH	15,016	331,372	180,949	3,0865	2,9596
17	NH ₂	16,024	168,615	188,522	-1,9835	3,8721
18	NH ₃	17,032	-46,191	192,137	-8,2828	4,8833
19	N ₂ H ₂	30,032	212,965	218,362	-8,9795	5,4752
20	N ₂ H ₃	31,040	153,971	228,513	-17,5062	6,9796
21	N ₂ H ₄	32,048	95,186	236,651	-25,3185	8,3608
22	C	12,011	715,003	157,853	6,4461	1,9977
23	CH	13,019	594,128	182,723	2,4421	3,,0829
24	HCN	27,027	130,540	201,631	-5,3642	4,6367

Properties for gases at $T_{ref} = 298,15 \text{ K}$

		M_i [kg/kmol]	$h_{i,m,ref}$ [kJ/mol]	$S_{i,m,ref}$ [kJ/mol K]	$\pi_{A,i}$	$\pi_{B,i}$
25	HCNO	43,027	-116,733	238,048	-10,1563	6,0671
26	HCO	29,019	-12,133	224,421	-,2313	4,2667
27	CH ₂	14,027	385,220	180,882	-5,6013	4,2667
28	CH ₂ O	30,027	-115,896	218,496	-8,5350	5,4012
29	CH ₃	15,035	145,686	193,899	-10,7155	5,3026
30	CH ₂ OH	31,035	-58,576	227,426	-15,3630	6,6590
31	CH ₄	16,043	-74,873	185,987	-17,6257	6,1658
32	CH ₃ OH	32,043	-200,581	240,212	-18,7088	7,3989
33	CO	28,011	-110,529	197,343	4,0573	3,1075
34	CO ₂	44,011	-393,522	213,317	-5,2380	4,8586
35	CN	26,019	456,056	202,334	4,6673	3,1075
36	C ₂	24,022	832,616	198,978	1,9146	3,5268

Properties for gases at $T_{ref} = 298,15 \text{ K}$

		M_i [kg/kmol]	$h_{i,m,ref}$ [kJ/mol]	$S_{i,m,ref}$ [kJ/mol K]	$\pi_{A,i}$	$\pi_{B,i}$
37	C ₂ H	25,030	476,976	207,238	-4,6242	4,6367
38	C ₂ H ₂	26,038	226,731	200,849	-15,3457	6,1658
39	C ₂ H ₃	27,046	279,910	227,861	-17,0316	6,9056
40	CH ₃ CO	43,046	-25,104	259,165	-24,2225	8,5334
41	C ₂ H ₄	28,054	52,283	219,468	-26,1999	8,1141
42	CH ₃ COH	44,054	-165,979	264,061	-30,7962	9,6679
43	C ₂ H ₅	29,062	110,299	228,183	-32,6833	9,2980
44	C ₂ H ₆	30,070	-84,667	228,781	-40,4718	10,4571
45	C ₃ H ₈	44,097	-103,847	269,529	-63,8077	14,7978
46	C ₄ H ₂	50,060	465,679	250,437	-34,0792	10,0379
47	C ₄ H ₃	51,068	455,847	273,424	-36,6848	10,8271
48	C ₄ H ₈	56,108	16,903	295,298	-72,9970	16,7215

Properties for gases at $T_{ref} = 298,15 \text{ K}$

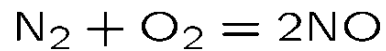
		M_i [kg/kmol]	$h_{i,m,ref}$ [kJ/mol]	$S_{i,m,ref}$ [kJ/mol K]	$\pi_{A,i}$	$\pi_{B,i}$
49	C_4H_{10}	58,124	-134,516	304,850	-86,8641	19,0399
50	C_5H_{10}	70,135	-35,941	325,281	-96,9383	20,9882
51	C_5H_{12}	72,151	-160,247	332,858	-110,2702	23,3312
52	C_6H_{12}	84,152	-59,622	350,087	-123,2381	25,5016
53	C_6H_{14}	86,178	-185,560	380,497	-137,3228	28,2638
54	C_7H_{14}	98,189	-72,132	389,217	-147,4583	29,6956
55	C_7H_{16}	100,205	-197,652	404,773	-162,6188	32,6045
56	C_8H_{16}	112,216	-135,821	418,705	-173,7077	34,5776
57	C_8H_{18}	114,232	-223,676	430,826	-191,8158	37,6111
58	C_2H_4O	44,054	-51,003	243,044	-34,3705	
59	HNO_3	63,016	-134,306	266,425	-19,5553	
60	He	4,003	0,000	125,800		

*Example 1: Equilibrium Calculation of the NO-air system

- Calculation of the equilibrium concentration [ppm] of NO in air
 - Temperatures up to 1500 K
 - $p = p_0 = 1 \text{ atm}$
 - Global reaction: $\text{N}_2 + \text{O}_2 = 2\text{NO}$

	π_{iA}	π_{iB}
N_2	3,6670	3,0582
O_2	4,1730	3,2309
NO	5,3476	3,1569

*Example 1: Equilibrium Calculation of the NO-air system



$$K_p = B_p T^{n_p} \exp\left(\frac{-\Delta h_{m,\text{ref}}}{RT}\right)$$

	π_{iA}	π_{iB}
N_2	3,6670	3,0582
O_2	4,1730	3,2309
NO	5,3476	3,1569

$$B_p = \exp\left(\sum_{i=1}^n \nu_i \pi_{i,A}\right) = \exp(2 \cdot 5,3476 - 3,6670 - 4,1730) = \exp(2,8552) = 17,38$$

$$n_p = \sum_{i=1}^n \nu_i \pi_{i,B} = 2 \cdot 3,1569 - 3,0582 - 3,2309 = 0,0247$$

*Example 1: Equilibrium Calculation of the NO-air system

$$\frac{\sum \nu_i h_{im_{ref}}}{R} = \frac{1}{8,3147} (2 \cdot 90,29 - 0 - 0) = 21719K$$

$$K_p(T) = 17,38 (T/K)^{0,0247} \exp\left(-\frac{21719}{T/K}\right)$$

- Law of mass action:
$$K_p = \prod_{i=1}^n \left(\frac{p_i}{p_0}\right)^{\nu_i}$$
- Assumption: $X_{O_2} = 0,21$, $X_{N_2} = 0,79$ (air) unchanged

$$p_{NO}^2 = p_{N_2} p_{O_2} K_p(T) = p^2 X_{N_2} X_{O_2} K_p(T)$$

$$X_{NO} = \frac{p_{NO}}{p} = 1,7(T/K)^{0,0124} \exp\left(-\frac{10860}{(T/K)}\right)$$

Result: Equilibrium Calculation of the NO-air system

Result:
$$X_{NO} = \frac{p_{NO}}{p} = 1,7(T/K)^{0,0124} \exp\left(-\frac{10860}{(T/K)}\right)$$

T [K]	X_{NO}	ppv
300	$3,52 \cdot 10^{-16}$	$3,52 \cdot 10^{-10}$
600	$2,55 \cdot 10^{-8}$	$2,55 \cdot 10^{-2}$
1000	$3,57 \cdot 10^{-5}$	35,7
1500	$1,22 \cdot 10^{-3}$	1220

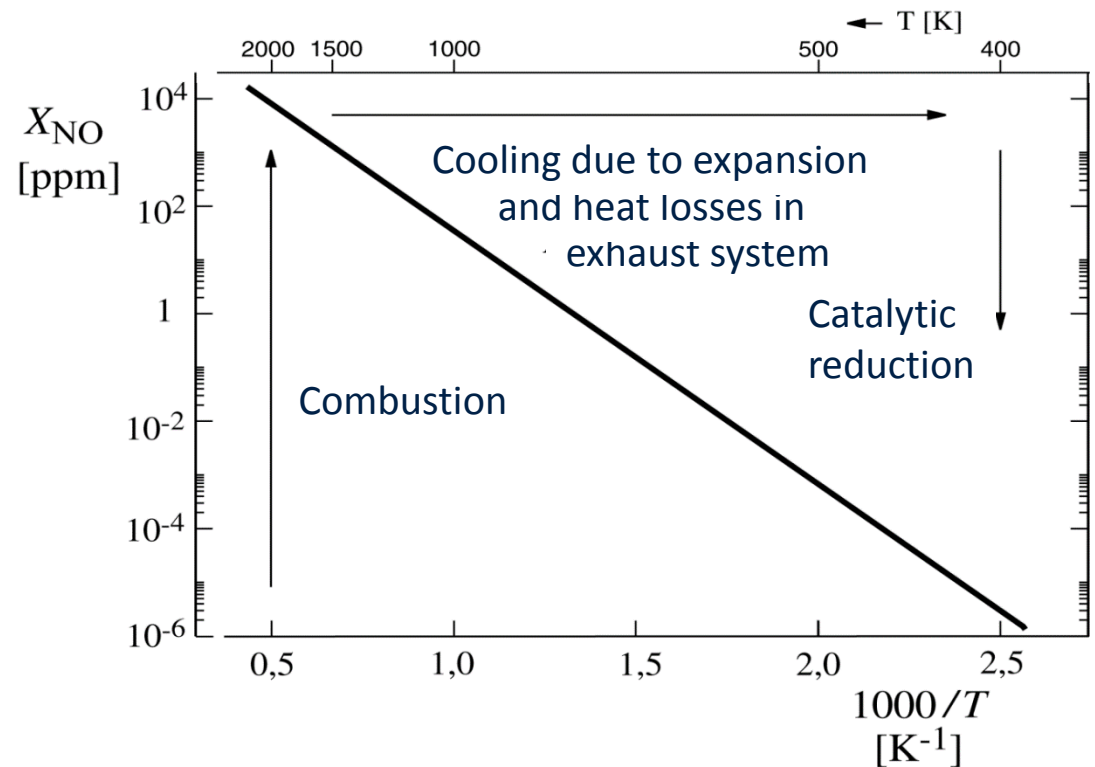
1 ppv = $10^{-6} = X_i \cdot 10^{-6}$ parts per million (volume fraction)

1 ppm = $10^{-6} = Y_i \cdot 10^{-6}$ parts per million (mass fraction)

$$Y_i = \frac{M_{NO}}{M_L} X_i = \frac{28}{28,8} X_i \approx X_i$$

Result: Equilibrium Calculation of the NO-air system

- Mole fraction of NO in equilibrium: $X_{\text{NO}} = 1,7 T^{0,0124} \exp(-10860/T)$
- Equilibrium values for $T = 2000 \text{ K}$ and $T = 400 \text{ K}$ differ by **10 orders of magnitude**
- **High temperatures** during combustion lead to **high NO-concentration**
- **NO is retained** to a large extent if gas is **cooled down rapidly**



*Example 2: Equilibrium Calculation of the H₂-air system

- Using the law of mass action one obtains for the reaction $2 \text{H}_2 + \text{O}_2 = 2 \text{H}_2\text{O}$ the relation between partial pressures

$$p_{\text{H}_2}^2 p_{\text{O}_2} = p_{\text{H}_2\text{O}}^2 K_{p1} \cdot p_{\text{O}},$$

where

$$K_{p1} = 0.0835 T^{-1.3565} \exp(58171/T)$$

was approximated using

$$K_{pl} = B_{pl} T^{n_{pl}} \exp\left(\frac{Q_{l,\text{ref}}}{\mathcal{R}T}\right), \quad l = 1, 2, \dots, r,$$

and the values for

$$B_{pl} = \exp\left(\sum_{i=1}^k \nu_{il} \pi_{iA}\right), \quad n_{pl} = \sum_{i=1}^k \nu_{il} \pi_{iB}, \quad l = 1, 2, \dots, r.$$

from the Janaf-Table

*Example 2: Equilibrium Calculation of the H₂-air system

- Introducing the definition

$$\Gamma_i = \frac{Y_i}{W_i}, \quad i = 1, 2, \dots, k$$

the partial pressures

$$p_i = pX_i, \quad i = 1, 2, \dots, k$$

are written with as

$$p_i = pX_i = p\Gamma_i W, \quad i = 1, 2, \dots, k,$$

where the mean molecular weight is

$$W = \left(\Gamma_{\text{H}_2} + \Gamma_{\text{O}_2} + \Gamma_{\text{H}_2\text{O}} + \Gamma_{\text{N}_2} \right)^{-1}.$$

*Example 2: Equilibrium Calculation of the H₂-air system

- The element mass fractions of the unburnt mixture are

$$Z_H = Y_{F,1}Z, \quad Z_O = Y_{O_2,2}(1-Z), \quad Z_N = Y_{N_2,2}(1-Z).$$

- These are equal to those in the equilibrium gas where

$$\frac{Z_H}{W_H} = 2\Gamma_{H_2,b} + 2\Gamma_{H_2O,b}$$

$$\frac{Z_O}{W_O} = 2\Gamma_{O_2,b} + \Gamma_{H_2O,b}$$

while Z_N remains unchanged

*Example 2: Equilibrium Calculation of the H₂-air system

- These equations lead to the following nonlinear equation for $\Gamma_{\text{H}_2\text{O},b}$

$$f(\Gamma_{\text{H}_2\text{O},b}) \equiv \left(\Gamma_{\text{H}_2\text{O},b} - \frac{Z_{\text{H}}}{2W_{\text{H}}} \right)^2 \left(\frac{Z_{\text{O}}}{W_{\text{O}}} - \Gamma_{\text{H}_2\text{O},b} \right)$$

$$-\frac{\Gamma_{\text{H}_2\text{O},b}^2}{K_{p1}^2} \left(\frac{Z_{\text{H}}}{W_{\text{H}}} + \frac{Z_{\text{O}}}{W_{\text{O}}} + 2\Gamma_{\text{N}_2} - \Gamma_{\text{H}_2\text{O},b} \right) = 0$$

*Example 2: Equilibrium Calculation of the H₂-air system

- Equation has one root between $\Gamma_{\text{H}_2\text{O},b} = 0$ and the maximum values

$$\Gamma_{\text{H}_2\text{O},b} = Z_{\text{H}}/2W_{\text{H}} \quad \text{and} \quad \Gamma_{\text{H}_2\text{O},b} = Z_{\text{O}}/W_{\text{O}}$$

which correspond to complete combustion for lean and rich conditions in the limit

$$K_{p1} \rightarrow \infty$$

- The solution, which is a function of the temperature, may be found by successively bracketing the solution within this range
- The temperature is then calculated by employing a Newton iteration on

$$h_u = h_b$$

leading to

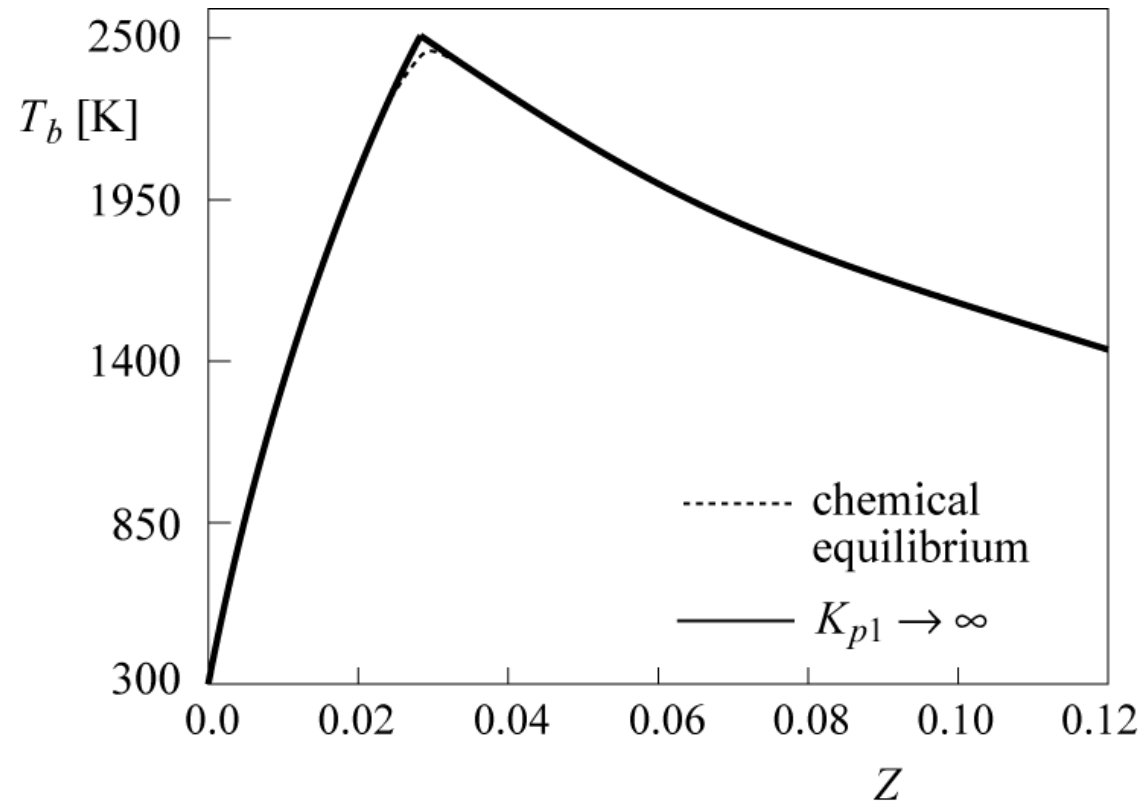
$$f_T(T) = h_u - \sum_{i=1}^k Y_{i,b} h_{i,\text{ref}} - \int_{T_{\text{ref}}}^T C_{p_b} dT.$$

*Example 2: Equilibrium Calculation of the H₂-air system

- The iteration converges readily following

$$T = T^i + \frac{f_T(T^i)}{C_{p_b}(T^i)}, \text{ where } i \text{ is the iteration index}$$

- The solution is plotted here for a hydrogen-air flame as a function of the mixture fraction for $T_u = 300$ K



Result: Equilibrium Calculation of the H₂-air system

- Equilibrium mass fractions of H₂, O₂ and H₂O
for $p = 1$ bar and $p = 10$ bar and different temperatures

T [K]	p [bar]	Y_{H_2}	Y_{O_2}	$Y_{\text{H}_2\text{O}}$
2000	1	0.0006	0.0049	0.9945
3000	1	0.0172	0.1364	0.8464
4000	1	0.0653	0.5180	0.4167
2000	10	0.0002	0.0022	0.9974
3000	10	0.0084	0.0664	0.9252
4000	10	0.0394	0.3127	0.6478

- $T \uparrow \rightarrow Y_{\text{H}_2\text{O}} \downarrow$
- $p \uparrow \rightarrow Y_{\text{H}_2\text{O}} \uparrow$

Conclusion: Pressure and temperature dependency of the equilibrium constant

- Temperature dependence

$$K_p = B_p T^{n_p} \exp\left(\frac{-\Delta h_{m,\text{ref}}}{RT}\right)$$

- Exothermic reactions: $\Delta h_{m,\text{ref}} < 0 \rightarrow dK_p/dT < 0$

- Equilibrium is shifted towards educts with increasing temperature

- Pressure dependence

$$\prod_{i=1}^n \left(\frac{p_i}{p_0}\right)^{\nu_{ik}} = K_{pk}(T)$$

- Less dissociation at higher pressure

- Le Chatelier's Principle

Equilibrium tries to counteract the imposed changes in temperature and pressure!

Summary

Part I: Fundamentals and Laminar Flames

- Introduction
- Fundamentals and mass balances of combustion systems
- Thermodynamics, flame temperature, and equilibrium
- Governing equations
- Laminar premixed flames: Kinematics and Burning Velocity
- Laminar premixed flames: Flame structure
- Laminar diffusion flames
- Thermodynamic quantities
- Flame temperature at complete conversion
- Chemical equilibrium