

Thermodynamics, Flame Temperature and Equilibrium

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
- FlameMaster flame calculator

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: $h = u + \frac{\mathcal{R}T}{M}$

- Energy balance for a closed system:

$$du = \delta q + \delta w$$

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

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

Multicomponent system

- Ideal gas
 - u and h **only function of temperature**

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

- If c_{pi} is specific heat 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 $h_{i,m}$ is

$$h_{i,m} = M_i h_i \quad i = 1, 2, \dots, k,$$

and its temperature dependence is

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

where the molar specific heat at constant pressure is

$$c_{pi,m} = M_i c_{pi} \quad i = 1, 2, \dots, k.$$

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

$$c_p = \sum_{i=1}^n Y_i c_{pi} \quad \left| \quad c_{p,m} = \sum_{i=1}^n X_i c_{pi,m} \right|$$

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 that CO_2 and H_2O are typically negative

Determination of Caloric Properties

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

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

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

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

- 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:	$300 < T < 1000$		
$a_1 = +0.3298\text{E}+01$	$a_2 = +0.8249\text{E}-03$	$a_3 = -0.8143\text{E}-06$	$a_4 = -0.9475\text{E} - 10$	
$a_5 = +0.4135\text{E}-12$	$a_6 = -0.1013\text{E}+04$	$a_7 = +0.3294\text{E}+01$		
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:	$300 < T < 1000$		
$a_1 = +0.3213\text{E}+01$	$a_2 = +0.1128\text{E}-02$	$a_3 = -0.5756\text{E}-06$	$a_4 = +0.1314\text{E} - 08$	
$a_5 = -0.8769\text{E}-12$	$a_6 = -0.1005\text{E}+04$	$a_7 = +0.6035\text{E}+01$		
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:	$300 < T < 1000$		
$a_1 = +0.3299\text{E}+01$	$a_2 = +0.1408\text{E}-02$	$a_3 = -0.3963\text{E}-05$	$a_4 = +0.5642\text{E} - 08$	
$a_5 = -0.2445\text{E}-11$	$a_6 = -0.1021\text{E}+04$	$a_7 = +0.3950\text{E}+01$		

Reaction Enthalpy

- First law of thermodynamics for a system at **constant pressure** ($dp = 0$)

- From first law $du = \delta q + \delta w$
it follows $dh = du + vdp + pdv = \delta q + vdp = \delta q$

- Heat release during combustion ($dp = 0$) given by reaction enthalpy:

$$\Delta h_m = \sum \nu_i h_{i,m}$$

- Stoichiometric coefficients:



- Reaction enthalpy: $\Delta h_m = h_{\text{CH}_4,m} + h_{\text{H}_2\text{O},m} - h_{\text{CO},m} - 3h_{\text{H}_2,m}$

Reaction Enthalpy

- Assumption that reaction occurs at $T = T_{\text{ref}}$, then

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

- Example CH_4 : $\text{C}(s) + 2\text{H}_2(g) = \text{CH}_4(g)$

$$\Delta h_{\text{CH}_4,m} = h_{\text{CH}_4,m,\text{ref}} - \underbrace{h_{\text{C},m,\text{ref}} - 2h_{\text{H}_2,m,\text{ref}}}_{=0} = h_{\text{CH}_4,m,\text{ref}}$$

- Example CO_2 : $\text{C}(s) + \text{O}_2(g) = \text{CO}_2(g)$

$$\Delta h_{\text{CO}_2,m} = h_{\text{CO}_2,m,\text{ref}}$$

- Example H_2O : $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) = \text{H}_2\text{O}(g)$

$$\Delta h_{\text{H}_2\text{O},m} = h_{\text{H}_2\text{O},m,\text{ref}}$$

- $h_{i,m,\text{ref}}$ is the chemical energy of a species with respect to $\text{H}_2(g)$, $\text{O}_2(g)$, $\text{N}_2(g)$, $\text{C}(s)$

List of enthalpies of formation

		M_i [kg/kmol]	$h_{i,m,ref}$ [kJ/mol]
1	H ₂	2,016	0.000
2	H ₂ O	18,016	-241,826
3	H ₂ O ₂	34,016	-136,105
4	NO	30,008	90,290
5	NO ₂	46,008	33,095
6	N ₂	28,016	0,000
7	N ₂ O	44,016	82,048
8	O	16,000	249,194
9	O ₂	32,000	0,000
10	O ₃	48,000	142,674

		M_i [kg/kmol]	$h_{i,m,ref}$ [kJ/mol]
11	CH ₂ O	30,027	-115,896
12	CH ₂ OH	31,035	-58,576
13	CH ₄	16,043	-74,873
14	CH ₃ OH	32,043	-200,581
15	CO	28,011	-110,529
16	CO ₂	44,011	-393,522
17	C ₂ H ₆	30,070	-84,667
18	C ₂ H ₄	28,054	52,283
19	C ₃ H ₈	44,097	-103,847

Reference temperature: $T_{ref} = 298,15 \text{ K}$

Reaction Enthalpy

- Classification of reactions:

- Exothermic reaction: $\Delta h_m < 0$

- Endothermic reaction: $\Delta h_m > 0$

- Lower heating value (LHV)

$$\text{LHV} = \frac{(-\Delta h_m)}{M_{\text{Fuel}}}$$

- Higher heating value (HHV)

$$\text{HHV} = \frac{(-\Delta h_m)}{M_{\text{Fuel}}} + \frac{M_{\text{H}_2\text{O}}}{2M_{\text{H}}} Z_{\text{Fuel},H} \cdot r = \frac{(-\Delta h_m)}{M_{\text{Fuel}}} + 8.937 \cdot Z_{\text{Fuel},H} \cdot 2442 \text{ kJ/kg}$$

- For CH_4 : HHV is $\sim 10\%$ larger than LHV

Example: Condensing Boiler



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GB312



The GB312 is available in the following kW outputs:

- 90kW
- 120kW
- 160kW
- 200kW
- 240kW
- 280kW

[Features](#)

[Further information](#)

[Controls and accessories](#)

[Technical data](#)

[Literature](#)

Servicing and maintenance

The GB312 is designed to make servicing and maintenance as straightforward as possible.

All parts can be accessed from the front and the burners can be accessed without having to disturb the gas connection.

The boiler is equipped with SAFe digital ignition technology and a Buderus Energy Management System (EMS).

Performance and design

The GB312 is a high performance, compact condensing boiler which provides an efficiency of up to 108% (NVC).

It can be fitted individually or as part of a 2 boiler cascade kit and is especially well suited to medium-large buildings and office blocks.

For a powerful floor standing condensing boiler it is very compact, lightweight and easy to install.

The boiler is whisper quiet, even when running at full output.

Quick links

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Enhanced Capital Allowance Scheme (ECA)


[ECA](#)

[...] efficiency of up to 108% (NVC).

Source:
Buderus

Course Overview

Part I: Fundamentals and Laminar Flames

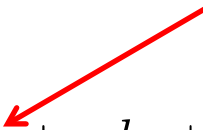
- Introduction
 - Fundamentals and mass balances of combustion systems
 - Thermodynamics, flame temperature, and equilibrium
 - Governing equations
 - Laminar premixed flames: Kinematics and burning velocity
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 - FlameMaster flame calculator
- Thermodynamic quantities
 - Flame temperature at complete conversion
 - 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 $\left. \frac{dY_i}{\nu_i M_i} = \frac{dY_1}{\nu_1 M_1} \quad (i = 1, 2, \dots, n) \right|$

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

$/ \times h_{i,\text{ref}}$

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

Flame Temperature at Complete Conversion

- Definition: **Heat of combustion**

$$Q = - \sum_{i=1}^k \nu_i M_i h_i = - \sum_{i=1}^k \nu_i h_{i,m}$$

- Heat of combustion changes very little with temperature

- Often set to:
$$Q_{\text{ref}} = - \sum_{i=1}^k \nu_i h_{i,m,\text{ref}}$$

- **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

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

- 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

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

→ **Coupling function between fuel mass fraction and temperature!**

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

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

Flame Temperature at Complete Conversion

- For a rich mixture

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

should be replaced by

$$Y_{i,u} - Y_{i,b} = (Y_{O_2,u} - Y_{O_2,b}) \frac{\nu_i M_i}{\nu_F M_F} \quad i = 1, 2, \dots, k$$

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

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

Flame Temperature at Complete Conversion

- Flame Temperature for **stoichiometric CH₄/air combustion** at T_u = 298 K:



$$Q_{\text{ref}} = -(h_{CO_2,m} + 2h_{H_2O,m} - h_{CH_4,m}) = 802.3 \text{ kJ/kg}$$

- Further Quantities:

$$Y_{F,u} = 0.0548 \quad c_p = 1.4 \text{ kJ/kg} \quad M_F = 0.016 \text{ kg/mol}$$

- Flame Temperature

$$T_b - T_u = \frac{Q_{\text{ref}} Y_{F,u}}{c_p \nu'_F M_F} \longrightarrow T_b = 2261K$$

- Determination of flame temperature from detailed thermodata models (no assumption for c_p)

$$T_b = 2225K \longrightarrow |\Delta T_b| = 36K$$

Flame Temperature at Complete Conversion

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

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

then take the form

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

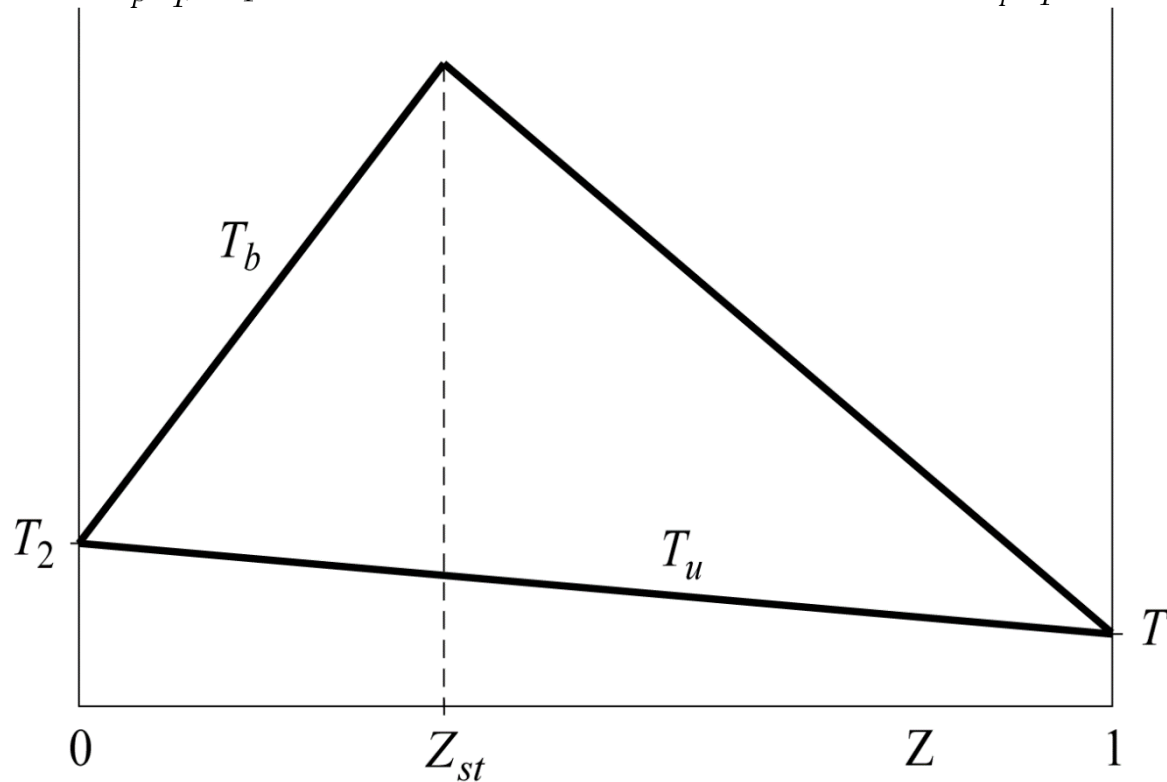
$$T_b(Z) = T_u(Z) + \frac{Q_{\text{ref}} Y_{O_2,1}}{c_p \nu'_F M_F} (1 - Z), \quad Z \geq Z_{st}$$

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

$$T_b(Z) = T_u(Z_{st}) + \frac{Q_{\text{ref}} Y_{F,1}}{c_p \nu'_F M_F} Z_{st} = T_u(Z_{st}) + \frac{Q_{\text{ref}} Y_{O_2,1}}{c_p \nu'_F M_F} (1 - Z_{st})$$

Flame Temperature at Complete Conversion

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



Burke-Schumann Solution:



Infinitely fast, irreversible one-step 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
 - 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

Entropy and Molar Entropy

- Partial molar **entropy** $s_{i,m}$ of chemical species in a mixture of ideal gases depends on **partial pressure**

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

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

$$s_{i,m}^0 = s_{i,m,\text{ref}}^0 + \int_{T_{\text{ref}}}^T \frac{c_{p,i,m}}{T} dT \quad i = 1, 2, \dots, k$$

depends only on temperature

- Values for the reference entropy $s_{i,m,\text{ref}}^0$ are listed in tables

- Gibbs Free Energy:

$$G = H - TS$$

– Part of energy that can be converted to work

- For mixtures with molar Gibbs Free Energy $g_{i,m}$

$$G = \sum_{i=1}^n n_i g_{i,m}$$

- Equilibrium, when Gibbs Free Energy reaches minimum, i.e. $dG = 0!$

- Gibbs equation for $G = G(p, T, n_i)$

$$dG = V dp - S dT + \sum_{i=1}^N \mu_i dn_i$$

- From Gibbs equation

$$dG = V dp - S dT + \sum_{i=1}^N \mu_i dn_i$$


and total differential of $G = G(p, T, n_j)$

$$dG = \left. \frac{\partial G}{\partial p} \right|_{T, \{n_i\}} dp + \left. \frac{\partial G}{\partial T} \right|_{p, \{n_i\}} dT + \sum_{i=1}^N \left. \frac{\partial G}{\partial n_i} \right|_{T, p, \{n_j, i \neq j\}} dn_i$$

follows $\left. \frac{\partial G}{\partial n_i} \right|_{T, p, \{n_j, i \neq j\}} = \mu_i$

- Since

$$G = \sum_{i=1}^n n_i g_{i,m}$$

 $\mu_i = g_{i,m}$

- Chemical potential is equal to partial molar Gibbs free energy

Chemical Potential and the Law of Mass Action

- Chemical potential

$$\mu_i = \quad = h_{i,m} - Ts_{i,m} = \mu_i^0(T) + \mathcal{R}T \ln \frac{p_i}{p_0} \quad i = 1, 2, \dots, k,$$

where

$$\mu_i^0 = h_{i,m,\text{ref}} - Ts_{i,m,\text{ref}} + \int_{T_{\text{ref}}}^T c_{p i,m} dT - T \int_{T_{\text{ref}}}^T \frac{c_{p i,m}}{T} dT \quad i = 1, 2, \dots, k$$

is chemical potential at 1 atm

- **Chemical equilibrium:** From $dG = 0 \quad \rightarrow \quad \sum_{i=1}^n \mu_i dn_i = \sum_{i=1}^n \nu_i \mu_i \frac{dn_i}{\nu_i} = 0$
- With coupling function, dn_i/n_i same for all species

$$\rightarrow \quad \frac{dn_i}{\nu_i} \sum_{i=1}^n \nu_i \mu_i = 0$$

\rightarrow

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

Chemical Potential and the Law of Mass Action

- Using $\mu_i = h_{i,m} - Ts_{i,m} = \mu_i^0(T) + \mathcal{R}T \ln \frac{p_i}{p_0} \quad i = 1, 2, \dots, k,$

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

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

Depends only on
thermodynamics,
not on composition

one obtains the **law of mass action**

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

Composition

Chemical potential and the law of mass action

- The law of mass action

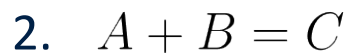
$$\prod_{i=1}^k \left(\frac{p_i}{p_0} \right)^{\nu_{il}} = K_{pl}(T), \quad l = 1, 2, \dots, r. \quad \leftarrow K_p \text{ only depends on temperature}$$

- Examples:



$$K_p(T) = \frac{p_C \cdot p_D}{p_A \cdot p_B} = \frac{X_C \cdot X_D}{X_A \cdot X_B}$$

→ K_p determines composition as a function of temperature:
 $\{X_i\} = f(T)$



$$K_p(T) = \frac{p_C}{p_A \cdot p_B} \cdot p_0 = \frac{X_C}{X_A \cdot X_B} \cdot \frac{p_0}{p}$$

→ K_p determines composition as a function of temperature and pressure:
 $\{X_i\} = f(T, p)$

Chemical potential and the law of mass action

- Law of mass action using K_p

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

- With the ideal gas law $p_i = C_i \mathcal{R}T$

follows

$$\prod_{i=1}^k C_i^{\nu_{il}} \cdot \left(\frac{\mathcal{R}T}{p_0} \right)^{(\sum_{j=1}^k \nu_{jl})} = K_{pl}(T)$$

- Law of mass action using K_C

$$\prod_{i=1}^k C_i^{\nu_{il}} = \frac{K_{pl}(T)}{\left(\frac{\mathcal{R}T}{p_0} \right)^{(\sum_{j=1}^k \nu_{jl})}} = K_{Cl}(T)$$

Chemical potential and the law of mass action

- Equilibrium for elementary reaction: $\nu'_A A + \nu'_B B \rightleftharpoons \nu'_C C + \nu'_D D$

$$\longrightarrow K_C(T) = \frac{C_C^{\nu''_C} C_D^{\nu''_D}}{C_A^{\nu'_A} C_B^{\nu'_B}}$$

- Rate of change $\frac{dC_A}{dt} = \nu_A (k_f C_A^{\nu'_A} C_B^{\nu'_B} - k_b C_C^{\nu''_C} C_D^{\nu''_D}) \stackrel{!}{=} 0$

$$\longrightarrow (k_f C_A^{\nu'_A} C_B^{\nu'_B})_{\text{eq}} = (k_b C_C^{\nu''_C} C_D^{\nu''_D})_{\text{eq}}$$

- For rate coefficients follows

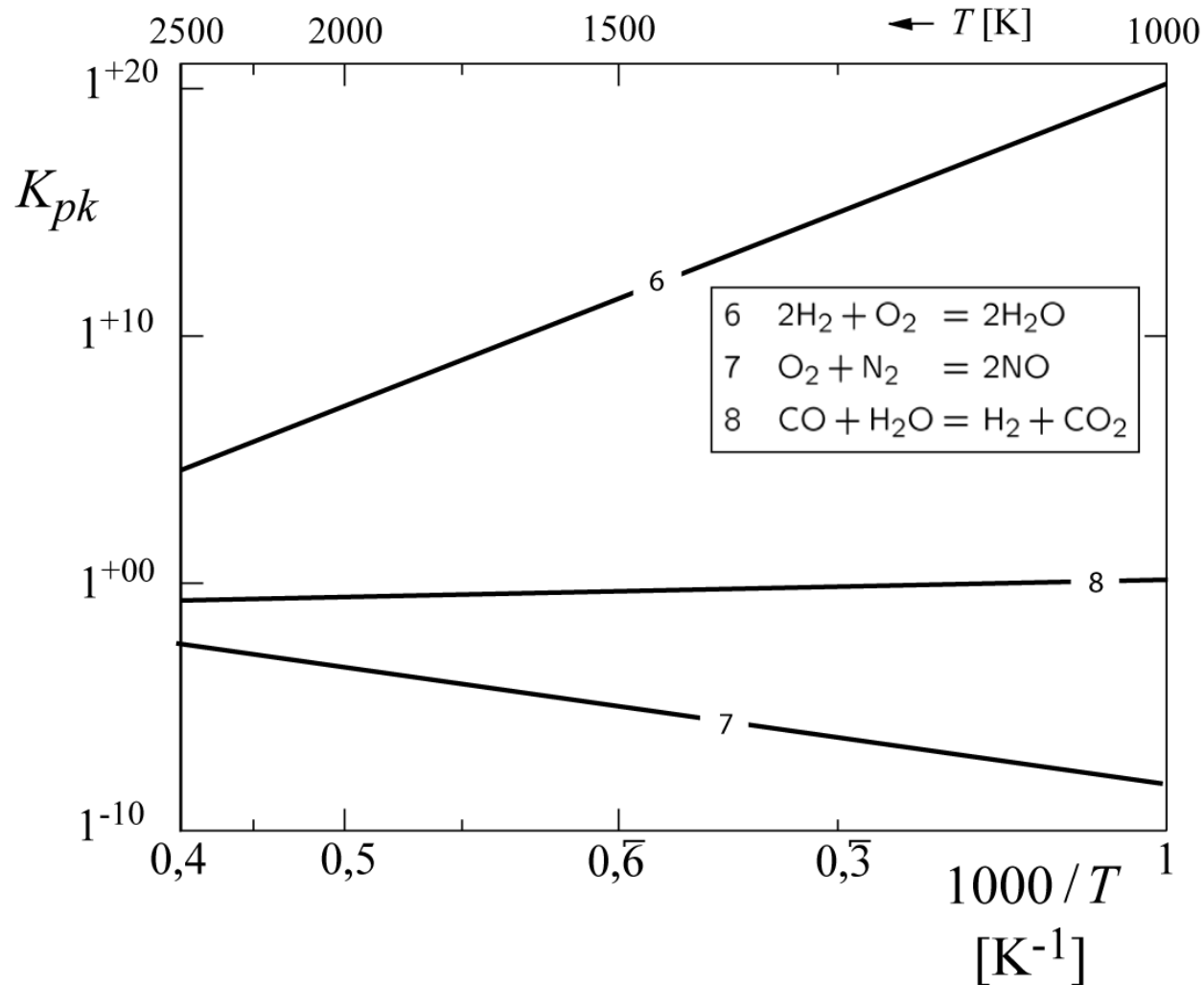
$$\frac{k_f(T)}{k_b(T)} = K_C(T) \quad \text{with} \quad K_C(T) = \frac{C_C^{\nu''_C} C_D^{\nu''_D}}{C_A^{\nu'_A} C_B^{\nu'_B}} \quad \text{and} \quad \boxed{K_C(T) = K_p(T) \cdot \left(\frac{p_0}{\mathcal{R}T}\right)^{\nu_s}}$$

\longrightarrow Equilibrium constant determines ratio of forward and reverse rate

\longrightarrow This is usually used to determine reverse from forward rate

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
 - Specific heats
- **Approximation**
 - Neglect temperature dependence of specific heats

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_2H	25,030	476,976	207,238	-4,6242	4,6367
38	C_2H_2	26,038	226,731	200,849	-15,3457	6,1658
39	C_2H_3	27,046	279,910	227,861	-17,0316	6,9056
40	CH_3CO	43,046	-25,104	259,165	-24,2225	8,5334
41	C_2H_4	28,054	52,283	219,468	-26,1999	8,1141
42	CH_3COH	44,054	-165,979	264,061	-30,7962	9,6679
43	C_2H_5	29,062	110,299	228,183	-32,6833	9,2980
44	C_2H_6	30,070	-84,667	228,781	-40,4718	10,4571
45	C_3H_8	44,097	-103,847	269,529	-63,8077	14,7978
46	C_4H_2	50,060	465,679	250,437	-34,0792	10,0379
47	C_4H_3	51,068	455,847	273,424	-36,6848	10,8271
48	C_4H_8	56,108	16,903	295,298	-72,9970	16,7215

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

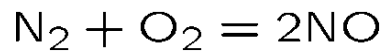
		M_i [kg/kmol]	$h_{i,m,ref}$ [kJ/mol]	$S_{i,m,ref}$ [kJ/mol K]	$\pi_{A,i}$	$\pi_{B,i}$
49	C_4H_{10}	58,124	-134,516	304,850	-86,8641	19,0399
50	C_5H_{10}	70,135	-35,941	325,281	-96,9383	20,9882
51	C_5H_{12}	72,151	-160,247	332,858	-110,2702	23,3312
52	C_6H_{12}	84,152	-59,622	350,087	-123,2381	25,5016
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:
$$X_{NO} = \frac{p_{NO}}{p} = 1,7(T/K)^{0,0124} \exp\left(-\frac{10860}{(T/K)}\right)$$

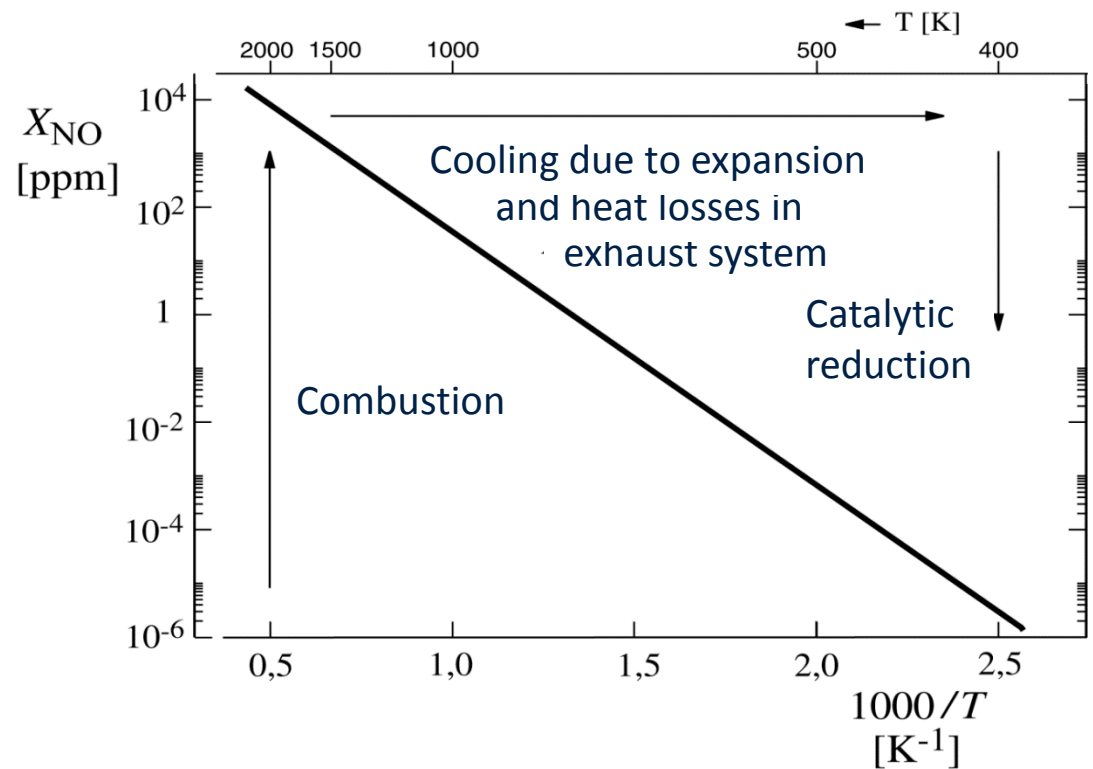
T [K]	X_{NO}	ppv
300	$3,52 \cdot 10^{-16}$	$3,52 \cdot 10^{-10}$
600	$2,55 \cdot 10^{-8}$	$2,55 \cdot 10^{-2}$
1000	$3,57 \cdot 10^{-5}$	35,7
1500	$1,22 \cdot 10^{-3}$	1220

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

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

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

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

the partial pressures

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

are written with as

$$p_i = p \frac{p_i}{p} = pX_i = p \frac{M}{M_i} Y_i = pM\Gamma_i \quad i = 1, 2, \dots, k,$$

where the mean molecular weight is

$$M = (\Gamma_{N_2} + \Gamma_{O_2} + \Gamma_{H_2O} + \Gamma_{H_2})^{-1}$$

*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

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

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

while Z_N remains unchanged

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

- These equations lead to the following nonlinear equation for $\Gamma_{H_2O,b}$

$$f(\Gamma_{H_2O,b}) = \left(\Gamma_{H_2O,b} - \frac{Z_H}{2M_H}\right)^2 \left(\frac{Z_O}{M_O} - \Gamma_{H_2O,b}\right) - \frac{\Gamma_{H_2O,b}^2}{K_{p1}^2 \cdot p} \left(\frac{Z_H}{M_H} + \frac{Z_O}{M_O} + 2\Gamma_{N_2} - \Gamma_{H_2O,b}\right) = 0$$

*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

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

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

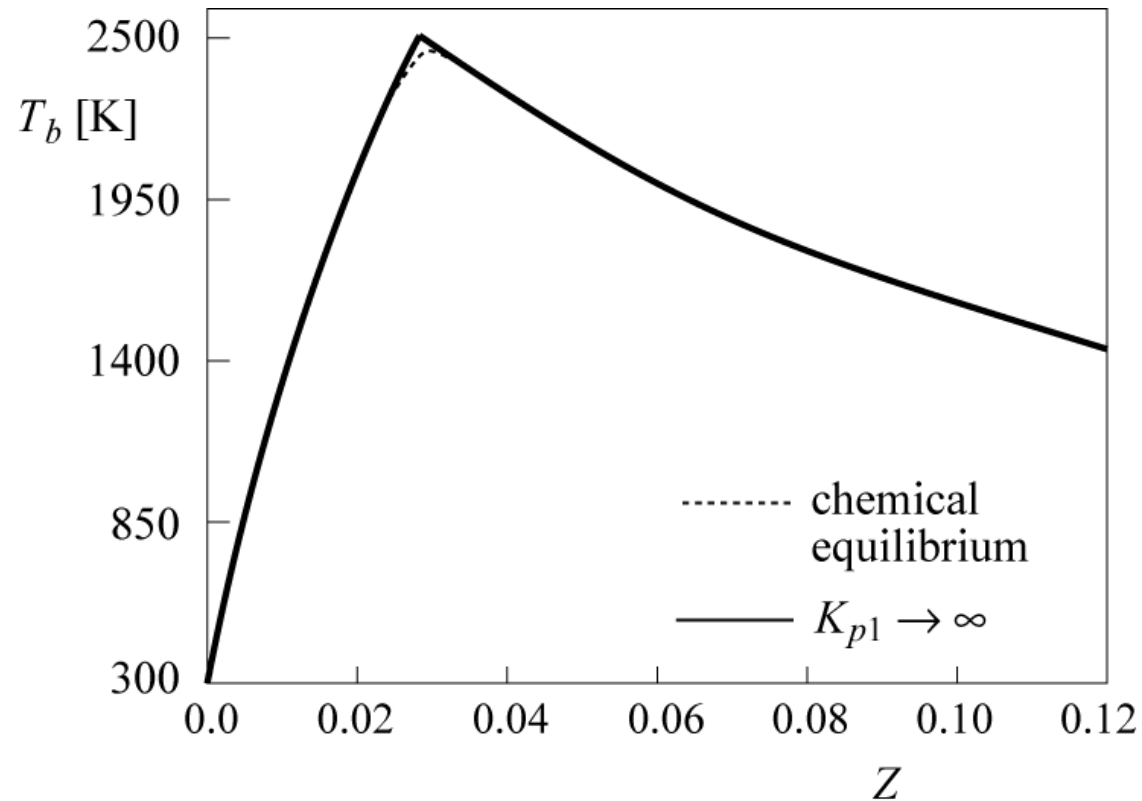
$$f_T(T) = h_u - \sum_{i=1}^k Y_{i,b} h_{i,\text{ref}} - \int_{T_{\text{ref}}}^T C_{p_b} dT.$$

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

- The iteration converges readily following

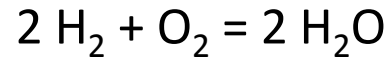
$$T = T^i + \frac{f_T(T^i)}{C_{p_b}(T^i)}, \text{ where } i \text{ is the iteration index}$$

- 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

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

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
- FlameMaster flame calculator
- Thermodynamic quantities
- Flame temperature at complete conversion
- Chemical equilibrium

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!