

Lecture 2

Flame Temperature and Chemical Equilibrium

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):
specific enthalpy for an ideal gas:
$$h = u + pv$$
$$h = u + \frac{\mathcal{R}T}{W}$$
- Energy balance: $du + pdv = dh - vdp = \delta q$

Multicomponent system

- The specific internal energy and specific enthalpy are the **mass-weighted** sums of the specific quantities of all species

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

- For an ideal gas the partial specific enthalpy is related to the partial specific internal energy by

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

- For an ideal gas internal energy and enthalpy depend only on temperature

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

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

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

- The reference temperature may be arbitrarily chosen, most frequently used:

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

- The **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

- The molar reference enthalpies of chemical species at reference temperature are listed in [tables](#)
- It should be noted that the 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

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

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

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

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

- The constants a_j for each species i are listed in tables

NASA Polynomials for two temperature ranges and standard pressure $p = 1$ atm

H₂	temperature range: $1000 < T < 5000$			
	$a_1 = +0.2991E+01$	$a_2 = +0.7000E-03$	$a_3 = -0.5634E-07$	$a_4 = -0.9232E - 11$
	$a_5 = +0.1583E-14$	$a_6 = -0.8350E+03$	$a_7 = -0.1355E+01$	
	temperature range: $300 < T < 1000$			
	$a_1 = +0.3298E+01$	$a_2 = +0.8249E-03$	$a_3 = -0.8143E-06$	$a_4 = -0.9475E - 10$
	$a_5 = +0.4135E-12$	$a_6 = -0.1013E+04$	$a_7 = +0.3294E+01$	
O₂	temperature range: $1000 < T < 5000$			
	$a_1 = +0.3698E+01$	$a_2 = +0.6135E-03$	$a_3 = -0.1259E-06$	$a_4 = +0.1775E - 10$
	$a_5 = -0.1136E-14$	$a_6 = -0.1234E+04$	$a_7 = +0.3189E+01$	
	temperature range: $300 < T < 1000$			
	$a_1 = +0.3213E+01$	$a_2 = +0.1128E-02$	$a_3 = -0.5756E-06$	$a_4 = +0.1314E - 08$
	$a_5 = -0.8769E-12$	$a_6 = -0.1005E+04$	$a_7 = +0.6035E+01$	
N₂	temperature range: $1000 < T < 5000$			
	$a_1 = +0.2927E+01$	$a_2 = +0.1488E-02$	$a_3 = -0.5685E-06$	$a_4 = +0.1010E - 09$
	$a_5 = -0.6753E-14$	$a_6 = -0.9228E+03$	$a_7 = +0.5981E+01$	
	temperature range: $300 < T < 1000$			
	$a_1 = +0.3299E+01$	$a_2 = +0.1408E-02$	$a_3 = -0.3963E-05$	$a_4 = +0.5642E - 08$
	$a_5 = -0.2445E-11$	$a_6 = -0.1021E+04$	$a_7 = +0.3950E+01$	

Flame Temperature at Complete Conversion

- First law of thermodynamics for an adiabatic system at constant pressure ($\delta q = 0, dp = 0$)

we neglect the work done by friction ($\delta w_R = 0$).

- From
$$dh - v dp = \delta q + \delta w_R$$

we then have:

$$dh = 0$$

- Integrated from the unburnt, index u , to the burnt state, index b , it follows:

$$h_u = h_b$$

or

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

- With the temperature dependence of the specific enthalpy

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

this may be written as

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

- Here the specific heat capacities are those of the mixture, to be calculated with the mass fractions of the burnt and unburnt gases

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

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

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

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

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

- Definition: Heat of combustion

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

- The heat of combustion changes very little with temperature

- It is often set equal 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, the contribution of nitrogen is dominant in calculating $c_{p,b}$
 - The value of c_{p_i} is somewhat larger for CO_2 and somewhat smaller for O_2 while that for H_2O is twice as large

- A first approximation for the specific heat of the burnt gas for lean and stoichiometric mixtures:

$$c_p = 1.40 \text{ kJ/kg/K}$$

- 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

$$\sum_{i=1}^k (Y_{i,u} - Y_{i,b}) h_{i,\text{ref}} = c_p (T_b - T_u)$$

and

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

with $\nu_F = -\nu'_F$ as

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

- For a rich mixture

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

must 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 ($Y_{O_2,b} = 0$)

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

- 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

- This equation describes mixing of the two streams with c_p assumed to be constant

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

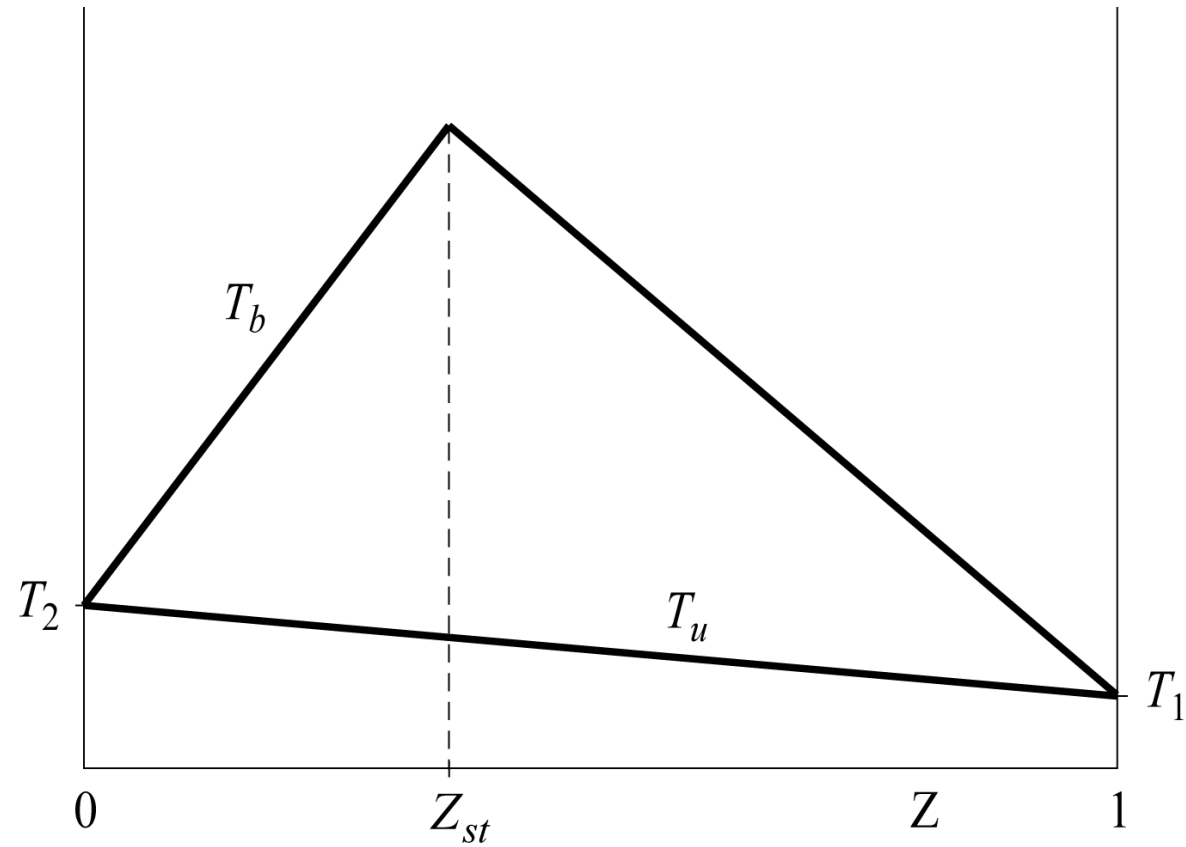
then take the form

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

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

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

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



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

- 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 ₂	0.07021	2686.7
C ₃ H ₈	0.06010	2289.7

Chemical Equilibrium

- The assumption of **complete combustion** is an approximation because it disregards the possibility of dissociation of combustion products
- A more general formulation is the assumption of **chemical equilibrium**
- Complete combustion represents the limit of an infinitely large equilibrium constant (see below)
- Chemical equilibrium and complete combustion are valid in the limit of infinitely fast reaction rates only, which will rarely be valid in combustion systems
- We will consider finite rate chemical kinetics in a later lecture

- Only for hydrogen diffusion flames complete chemical equilibrium is a good approximation, while for hydrocarbon diffusion flames finite kinetic rates are needed
- In hydrocarbon diffusion flames, the fast chemistry assumption overpredicts the formation of intermediates such as CO and H₂ due to the dissociation of fuel on the rich side by large amounts
- Nevertheless, since the equilibrium assumption represents an exact thermodynamic limit, it shall be considered here

Chemical potential and the law of mass action

- Differently from the enthalpy, the partial molar entropy S_i of a chemical species in a mixture of ideal gases depends on the 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 $S_{i,\text{ref}}^0$ are also listed in tables

- The partial molar entropy may now be used to define the 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

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

is the chemical potential at 1 atm

- The condition for chemical equilibrium for the l -th reaction is given by

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

- 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

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

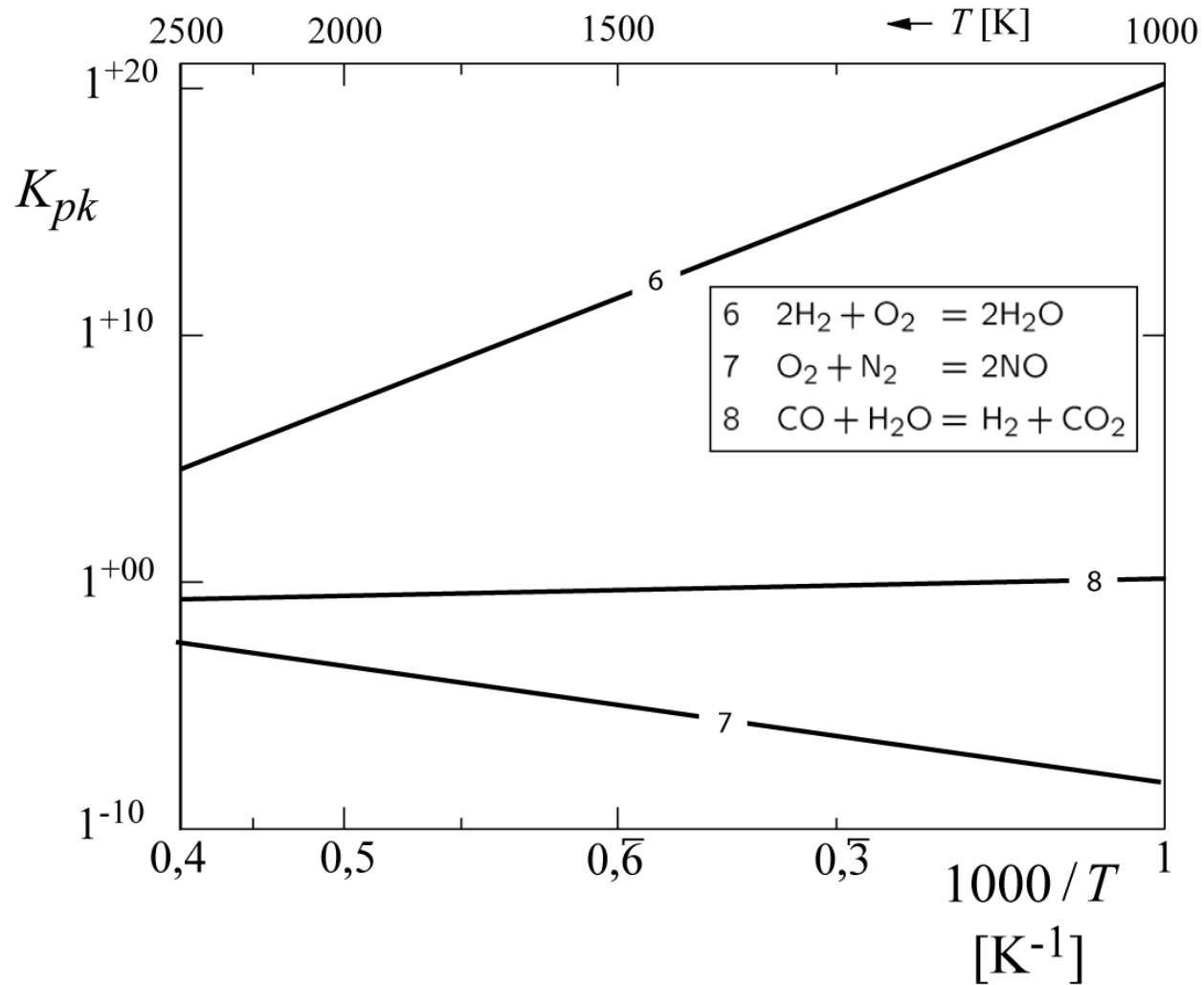
- Defining the equilibrium constant K_{pl} by

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

one obtains the [law of mass action](#)

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

- Equilibrium constants for three reactions



Approximation and Simple Calculation of Chemical Equilibria

- An approximation of equilibrium constants may be derived by introducing the quantity

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

- For constant C_{p_i} the second term in this expression would yield a logarithm of the temperature, while the last term does not vary much if $T \gg T_{\text{ref}}$
- Therefore $p_i(T)$ may be approximated by

$$\pi_i(T) = \pi_{iA} + \pi_{iB} \ln T, \quad i = 1, 2, \dots, k.$$

- Introducing this into

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

one obtains

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

where

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

was used and

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

- Values for π_{iA} and π_{iB} were obtained by linear interpolation in terms of $\ln T$ for the values given in the JANAF-Tables at $T = 300$ K and $T = 2000$ K.
- For some species, which are important in combustion, values for π_{iA} and π_{iB} are listed in Tab. 2.1 of the lecture notes.

Excerpt of Tab. 2.1:

Nr.	species	M_i kg/kmol	$H_{i,ref}$ kJ/mol	$S_{i,ref}$ kJ/(molK)	$\pi_{A,i}$	$\pi_{B,i}$
1	H	1.008	217.986	114.470	-1.2261	1.9977
3	OH	17.008	39.463	183.367	3.3965	2.9596
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
9	NO	30.008	90.290	210.442	5.3476	3.1569
11	NN	28.016	0.000	191.300	3.6670	3.0582
13	O	16.000	249.194	160.728	6.8561	1.9977
14	O ₂	32.000	0.000	204.848	4.1730	3.2309
29	CH ₃	15.035	145.686	193.899	-10.7155	5.3026
31	CH ₄	16.043	-74.873	185.987	-17.6257	6.1658
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
41	C ₂ H ₄	28.054	52.283	219.468	-26.1999	8.1141
57	C ₈ H ₁₈	114.232	-223.676	430.826	-191.8158	37.6111
62	C _{solid}	12.011	0.000	0.000	-9.975	1.719

An example: 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.

- Introducing the definition

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

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

are written with as

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

where the mean molecular weight is

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

- 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.

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

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

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

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

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

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

$$h_u = h_b$$

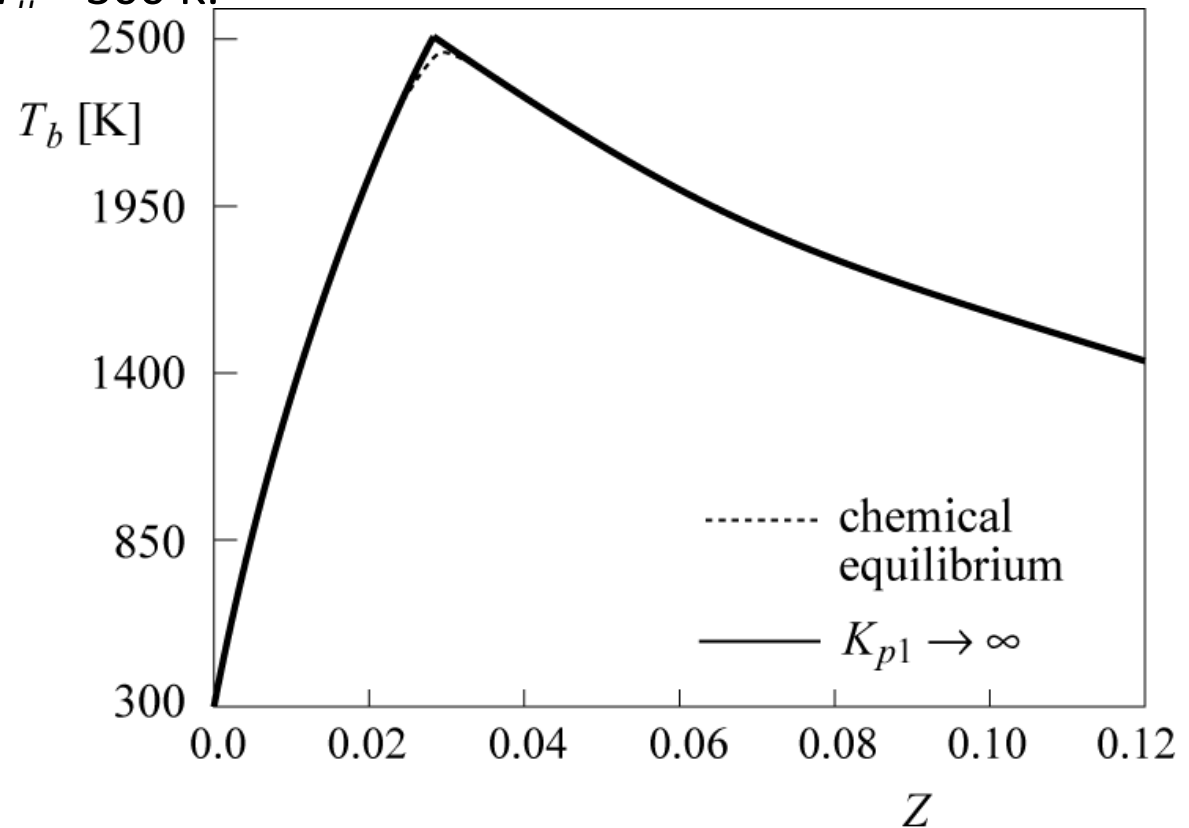
$$f_T(T) = h_u - \sum_{i=1}^k Y_{i,b} h_{i,\text{ref}} - \int_{T_{\text{ref}}}^T C_{p_b} dT.$$

leading to

- The iteration converges readily following

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

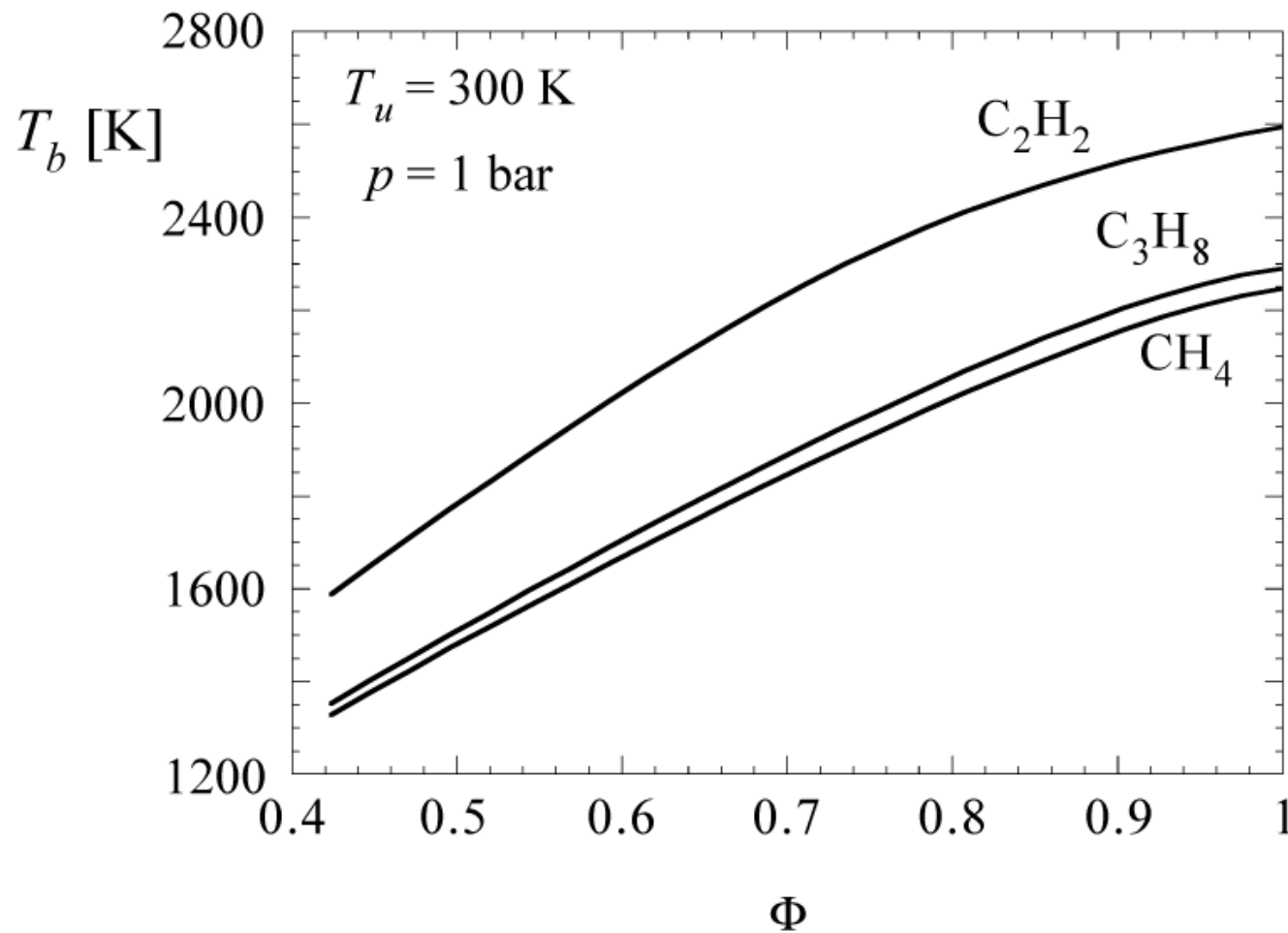
- The solution is plotted here for a hydrogen-air flame as a function of the mixture fraction for $T_{\infty} = 300$ K.



- The table shows equilibrium mass fractions of H_2 , O_2 and H_2O for $p=1$ bar and $p=10$ bar and different temperatures

T [K]	p [bar]	Y_{H_2}	Y_{O_2}	Y_{H_2O}
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

- Equilibrium temperature profiles for lean methane, acetylene and propane flames as a function of the equivalence ratio for $T_u = 300$ K



The heterogeneous equilibrium

- A reaction is called heterogeneous, if it occurs for instance at the gas-to-solid interface.
- Since the chemical potential of the solid is independent of pressure

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

only the partial pressures of the gaseous components will appear in the law of mass action.

- Example: the reaction of solid carbon with oxygen $C_s + O_2 = CO_2$
- The ratio of partial pressures of CO_2 and O_2 becomes

$$\frac{p_{CO_2}}{p_{O_2}} = \exp\left(\frac{\mu_{CO_2}^0 - \mu_{C_s}^0 - \mu_{O_2}^0}{RT}\right) = K_p.$$

- Here the molar enthalpy $H_{C_s, \text{ref}}$ of solid carbon is zero per definition, while $\pi_{A, C_s} = -9.979$ and $\pi_{B, C_s} = 1.719$

Example

- Calculate the equilibrium mole fraction of NO in air at $T = 1000$ K and $T = 1500$ K by assuming that the mole fractions of O_2 ($X_{O_2} = 0.21$) and N_2 ($X_{N_2} = 0.79$) remain unchanged.

Solution

- The equilibrium constant of the reaction $N_2 + O_2 = 2 NO$ is with the values of the JANAF Table

$$K_p(T) = 17.38 T^{0.0247} \exp(-21719/T)$$

- For the partial pressure of NO one has

$$p_{\text{NO}} = (p_{\text{N}_2} p_{\text{O}_2} K_p)^{1/2}$$

- Neglecting the consumption of N_2 and O_2 as a first approximation, their partial pressures in air may be approximated as

$$p_{\text{N}_2} = 0.79 p, \quad p_{\text{O}_2} = 0.21 p$$

- The equilibrium mole fraction of NO is then

$$X_{\text{NO}} = 1.7 T^{0.01235} \exp(-10856/T).$$

- At $T = 1000$ K one obtains 38 ppv (parts per volume = $X_i \cdot 10^6$) and at $T = 1500$ K 230 ppv.

- This indicates that at high temperatures equilibrium NO-levels exceed by far those that are accepted by modern emission standards which are around 100 ppv or lower.
- Equilibrium considerations therefore suggest that in low temperature exhaust gases NO is above the equilibrium value and can be removed by catalysts.