# Lecture 2

## Adiabatic Flame Temperature

## and

## Chemical Equilibrium

**First law of thermodynamics** - balance between different forms of energy

change of specific internal energy: $\mathrm{d}u$

specific work due to volumetric changes: $\delta w^{\mathrm{rev}} = p\,\mathrm{d}v,\ v = 1/\rho$

specific heat transfer from the surroundings: $\delta q$

specific frictional work: $\delta w_R$ [*]

Related quantities

specific enthalpy (general definition): $h = u + pv$

specific enthalpy for an ideal gas: $h = u + \dfrac{\mathcal{R}T}{W}$

Energy balance: $\mathrm{d}u + p\,\mathrm{d}v = \mathrm{d}h - v\,\mathrm{d}p = \delta q + \delta w_R$

[*] The list of energies is not exhaustive, f. e. work of forces and kinetic or potential energies are missing, but the most important which will appear in a balance are considered here.

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# 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 the inner energy and enthalpy depend on temperature alone.

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

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

the temperature dependence of the partial specific enthalpy is given by

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

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 is

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

and its temperature dependence is

$$H_i = H_{i,\mathrm{ref}} + \int_{T_{\mathrm{ref}}}^{T} C_{pi}\mathrm{d}T, \quad i = 1, 2, \ldots, k,$$

where the molar heat capacity at constant pressure is

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

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

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

The molar reference enthalpies at reference temperature of species 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 the NASA polynomials.

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

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

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

The constants $a_j$ for each species $i$ are listed in tables.

First law of thermodynamics for an adiabatic system at constant pressure
($\delta q = 0$, $\mathrm{d}p = 0$)

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

$$\mathrm{d}h - v\mathrm{d}p^{\,0} = \delta q^{\,0} + \delta w_R^{\,0}$$

we then have:

$$\mathrm{d}h = 0$$

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

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

this may be written as

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

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

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

may be calculated by integrating $\dfrac{\text{d}Y_i}{\nu_i W_i} = \dfrac{\text{d}Y_1}{\nu_1 W_1}, \quad i = 2,\dots,k$

which gives

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

such that

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

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 $c_{pi}$ 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 adiabatic flame temperature 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

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

must be replaced by

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

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

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

Equations $\qquad T_b - T_u = \dfrac{Q_{\mathsf{ref}} Y_{\mathsf{F},u}}{c_p \nu'_{\mathsf{F}} W_{\mathsf{F}}} \qquad$ and $\qquad T_b - T_u = \dfrac{Q_{\mathsf{ref}} Y_{\mathsf{O}_2,u}}{c_p \nu'_{\mathsf{O}_2} W_{\mathsf{O}_2}}$

may be expressed in terms of the mixture fraction.

Introducing $\qquad Y_{\mathsf{F},u} = Y_{\mathsf{F},1} Z \qquad$ and $\qquad Y_{\mathsf{O}_2,u} = Y_{\mathsf{O}_2,2}(1 - Z)$

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
$$T_b - T_u = \frac{Q_{\mathsf{ref}} Y_{\mathsf{F},u}}{c_p \nu'_{\mathsf{F}} W_{\mathsf{F}}} \qquad \text{and} \qquad T_b - T_u = \frac{Q_{\mathsf{ref}} Y_{\mathsf{O_2},u}}{c_p \nu'_{\mathsf{O_2}} W_{\mathsf{O_2}}}$$
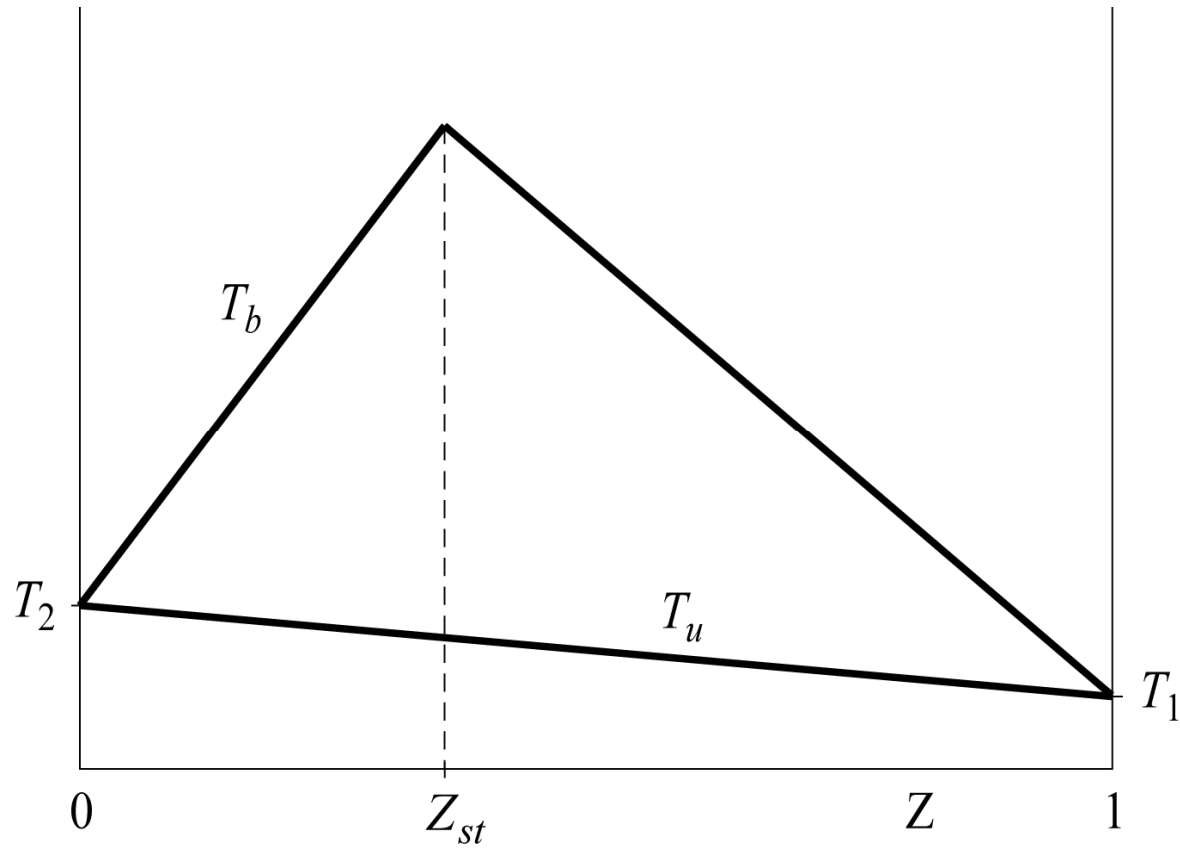
then take the form

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

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

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

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

$$T_b(Z) = T_u(Z) + \frac{Q_{\mathrm{ref}} Y_{\mathsf{F},1}}{c_p \nu'_{\mathsf{F}} W_{\mathsf{F}}} Z, \quad Z \le Z_{st}, \quad T_b(Z) = T_u(Z) + \frac{Q_{\mathrm{ref}} Y_{\mathsf{O}_2,2}}{c_p \nu'_{\mathsf{O}_2} W_{\mathsf{O}_2}} \left(1 - Z\right) \quad Z \ge Z_{st}$$

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In the table for combustion of a pure fuels ($Y_{F,1} = 1$) in air ($Y_{O2,2} = 0.232$) with $T_{u,st} = 300$ K and $c_p = 1.4$ kJ/kg/K

stoichiometric mixture fractions and stoichiometric flame temperatures for some hydrocarbon-air mixtures are shown.

| Fuel | $Z_{st}$ | $T_{st}$ [K] |
|------|----------|--------------|
| $CH_4$ | 0.05496 | 2263.3 |
| $C_2H_6$ | 0.05864 | 2288.8 |
| $C_2H_4$ | 0.06349 | 2438.5 |
| $C_2H_4$ | 0.07021 | 2686.7 |
| $C_3H_8$ | 0.06010 | 2289.7 |

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**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 infinite equilibrium constant (see below).

Chemical equilibrium and complete combustion are valid in the limit of infinitely fast reaction rates only, which will seldom 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 $H_2$ 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

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

where $p_0 = 1$ atm and

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

depends only on temperature.

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

The partial molar entropy may now be used to define the chemical potential

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

where

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

is the chemical potential at 1 atm.

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

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

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

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

leads to
$$-\sum_{i=1}^{k} \nu_{il} \mu_i^0 = \mathcal{R}T \ln \prod_{i=1}^{k} \left( \frac{p_i}{p_0} \right)^{\nu_{il}}, \quad l = 1, 2, \ldots, r.$$
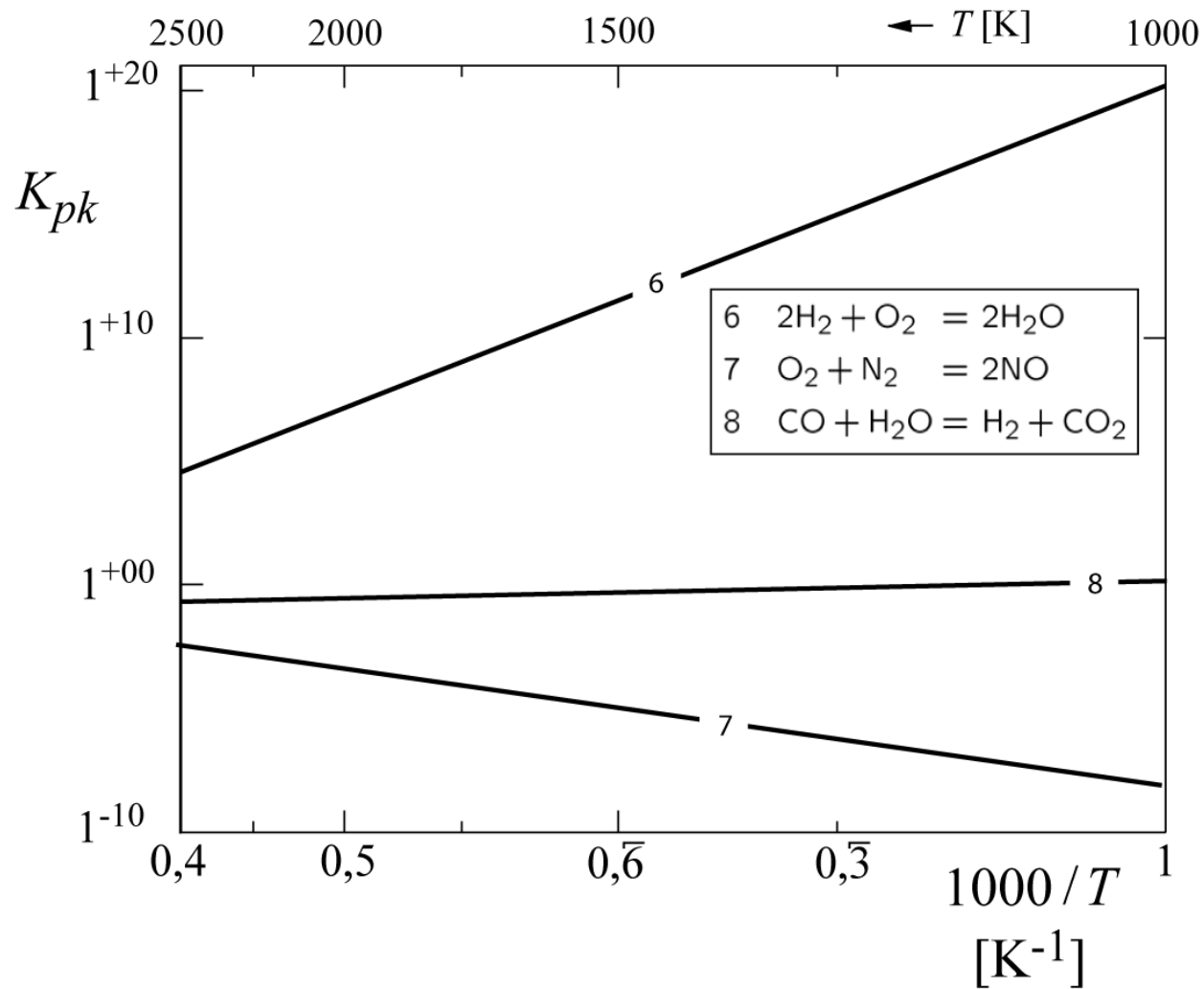
Defining the equilibrium constant $K_{pl}$ by
$$\mathcal{R}T \ln K_{pl} = -\sum_{i=1}^{k} \nu_{il} \mu_i^0, \quad l = 1, 2, \ldots, r$$

one obtains the law of mass action
$$\prod_{i=1}^{k} \left( \frac{p_i}{p_0} \right)^{\nu_{il}} = K_{pl}(T), \quad l = 1, 2, \ldots, r.$$

# Equilibrium constants for three reactions

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

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

For constant $C_{pi}$ 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 $\pi_i(T)$ may be approximated by

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

Introducing this into

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

one obtains

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

where

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

was used and

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

Values for $\pi_{iA}$ and $\pi_{iB}$ 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 $\pi_{iA}$ and $\pi_{iB}$ are listed in Tab. 2.1 of the lecture notes.

Excerpt of Tab. 2.1:

| Nr. | species | $M_i$ | $H_{i,\text{ref}}$ | $S_{i,\text{ref}}$ | $\pi_{A,i}$ | $\pi_{B,i}$ |
|---|---|---|---|---|---|---|
| | | kg/kmol | kJ/mol | kJ/(molK) | | |
| 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 | $H_2O$ | 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 | $C_2H_4$ | 28.054 | 52.283 | 219.468 | -26.1999 | 8.1141 |
| 57 | $C_8H_{18}$ | 114.232 | -223.676 | 430.826 | -191.8158 | 37.6111 |
| 62 | $C_{\text{solid}}$ | 12.011 | 0.000 | 0.000 | -9.975 | 1.719 |

# An example: Equilibrium Calculation of the $H_2$-air system

Using the law of mass action one obtains for the reaction $\quad 2\,H_2 + O_2 = 2\,H_2O$
the relation between partial pressures

$$p_{H_2}^2 p_{O_2} = p_{H_2O}^2 K_{p1} \cdot p_O,$$

where

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

was approximated using

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

and the values for

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

from the Janaf-Table.

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Introducing the definition

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

the partial pressures

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

are written with as

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

where the mean molecular weight is

$$W = \left( \Gamma_{H_2} + \Gamma_{O_2} + \Gamma_{H_2O} + \Gamma_{N_2} \right)^{-1}.$$

The element mass fractions of the unburnt mixture are

$$Z_\text{H} = Y_{\text{F},1}Z, \quad Z_\text{O} = Y_{\text{O}_2,2}(1-Z), \quad Z_\text{N} = Y_{\text{N}_\text{@},2}(1-Z).$$

These are equal to those in the equilibrium gas where

$$\frac{Z_\text{H}}{W_\text{H}} = 2\Gamma_{\text{H}_2,b} + 2\Gamma_{\text{H}_2\text{O},b}$$

$$\frac{Z_\text{O}}{W_\text{O}} = 2\Gamma_{\text{O}_2,b} + \Gamma_{\text{H}_2\text{O},b},$$

while $Z_\text{N}$ remains unchanged.

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

$$f(\Gamma_{H_2O,b}) \equiv \left(\Gamma_{H_2O,b} - \frac{Z_H}{2W_H}\right)^2 \left(\frac{Z_O}{W_O} - \Gamma_{H_2O,b}\right)$$

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

This equation has one root between $\Gamma_{\text{H2O},b} = 0$ and the maximum values

$$\Gamma_{\text{H2O},b} = Z_{\text{H}}/2W_{\text{H}} \text{ and } \Gamma_{\text{H2O},b} = Z_{\text{O}}/W_{\text{O}}$$

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

$$K_{p1} \to \infty$$

The solution, which is a function of the temperature, may be found by successively bracketing the solution within this range.

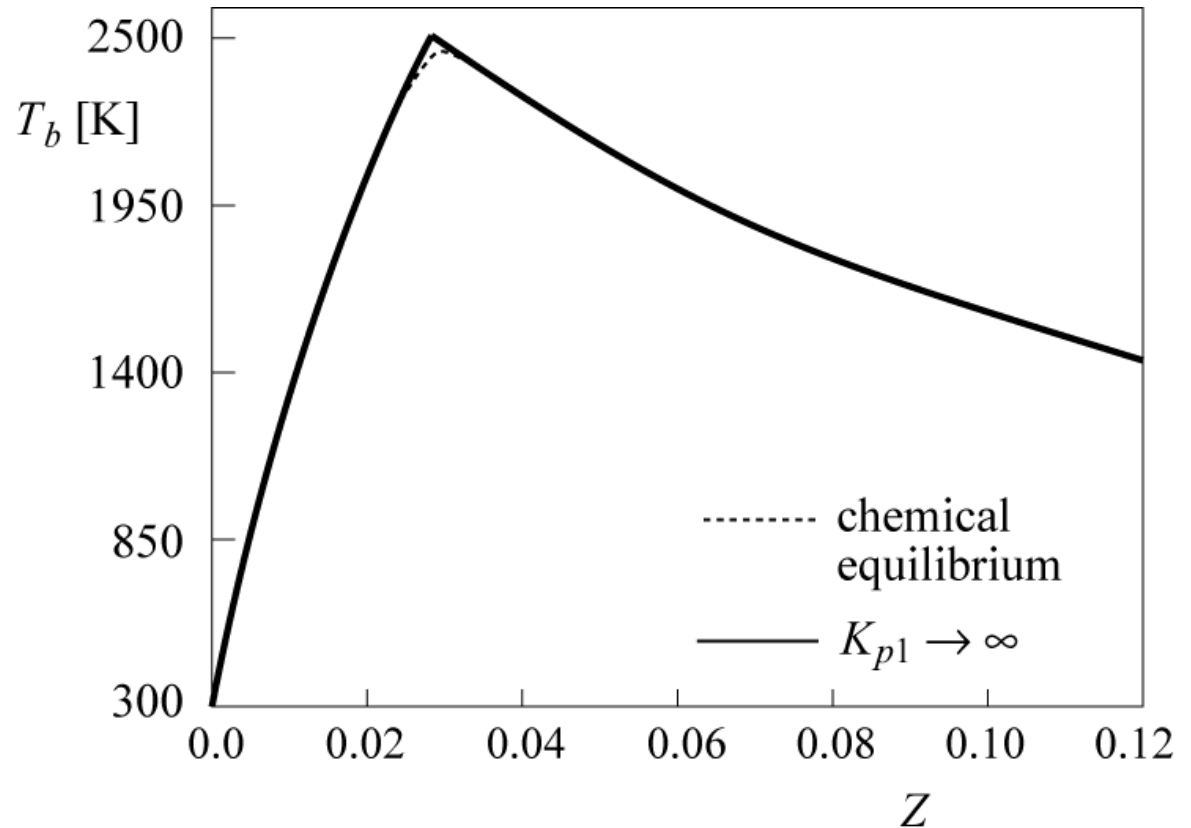The temperature is then calculated by employing a Newton iteration on

$$h_u = h_b$$

leading to

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

The iteration converges readily following

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

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

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 |

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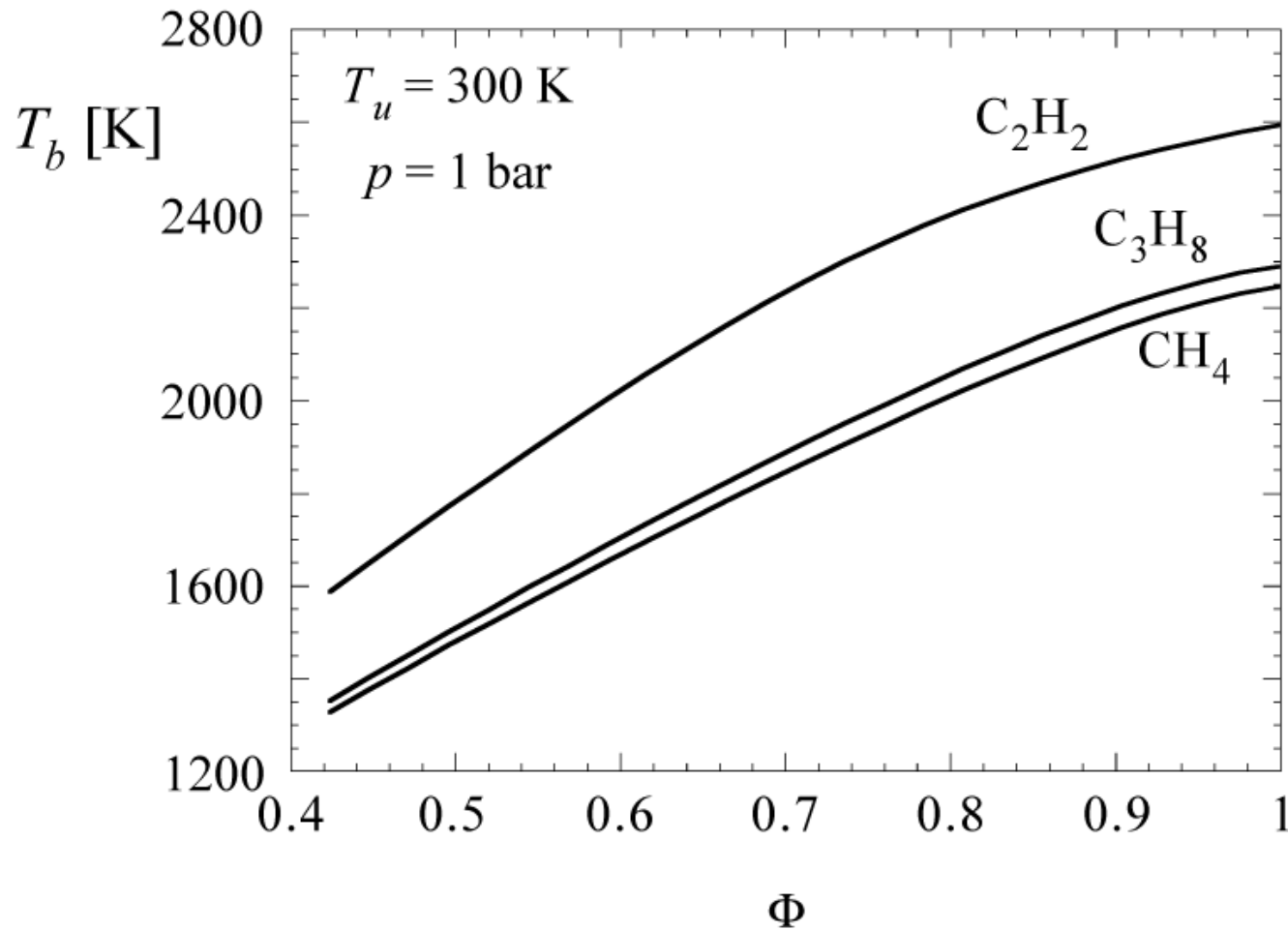
**The heterogeneous equilibrium**

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

$$\mu_i = \mu_i^0 = H_{i,\mathrm{ref}} - TS_{i,\mathrm{ref}} + \int\limits_{T_{\mathrm{ref}}}^{T} C_{p,i}\,\mathrm{d}T - T\int\limits_{T_{\mathrm{ref}}}^{T} \frac{C_{p,i}}{T}\,\mathrm{d}T, \quad i = 1, 2, \ldots, k$$

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

Example: the reaction of solid carbon with oxygene $C_s + O_2 = CO_2$

The ratio of partial pressures of $CO_2$ and $O_2$ becomes

$$\frac{p_{CO_2}}{p_{O_2}} = \exp\left(\frac{\mu^0_{CO_2} - \mu^0_{C_s} - \mu^0_{O_2}}{\mathcal{R}T}\right) = K_p.$$

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

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

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 $= X_i\ 10^{-6}$) 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.