Jet and Rocket Propulsion

AE4451

LECTURE 7

Sedina Tsikata – January 25, 2023

Overview

what we saw last time:

E_{chem}

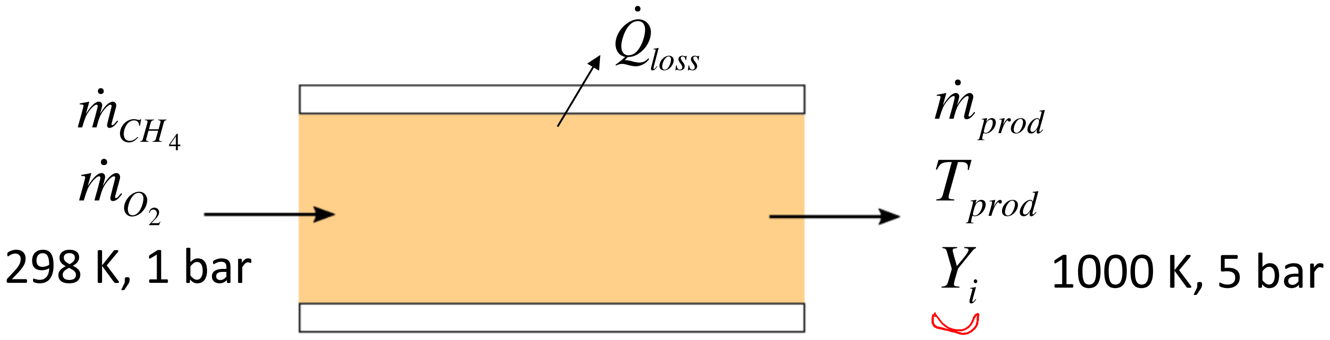
- chemical equilibrium thermodynamics
  - - chemical transformations: addition of Echem to enthalpy terms
  - - enthalpy-temperature diagrams and reaction pathways
  - - heat of reaction, heat of formation

today:

- complete combustor example
- chemical equilibrium thermodynamics continued: product composition

Example

Case of a methane-oxygen combustor



- gaseous methane and oxygen entering non-adiabatic combustor at 298 K, 1 bar (stagnation conditions)
- mass flowrate of oxygen is 5× that for methane
- heat loss results in 1000 K product temperature

Q. what is the heat loss rate per unit mass flow rate, $\dot{Q}_{loss}/\dot{m}$?

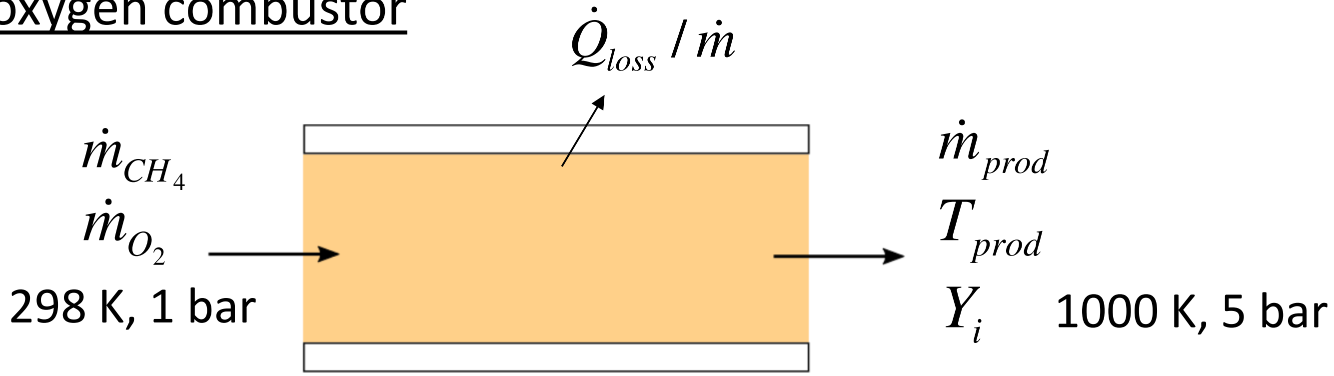
$pV = nRT$ $\qquad$ $c_p, c_v \neq$ constant

assume:

steady state, no “shaft” work, thermally perfect but not calorically perfect gases

Example

Case of a methane-oxygen combustor



1. mass conservation

$$\underline{\dot{m}_{in} = \dot{m}_{exit}} \equiv \dot{m}$$

$$\boxed{\dot{Q}_{in} - \cancel{\dot{W}_{shaft}} + \cancel{\int_{CV} \rho \vec{f} \cdot \vec{u}\, dV} - \int_{CS} p\left(\vec{u} - \cancel{\vec{u}_{rel}}\right) \cdot \hat{n}\, dA = \cancel{\frac{d}{dt} \int_{CV} \rho e_o\, dV} + \int_{CS} \rho h_o \left(\vec{u}_{rel} \cdot \hat{n}\right) dA}$$

2. energy conservation

$$\dot{m} h_{o,in} = \underline{\dot{m} h_{o,exit} + \dot{Q}_{loss}}$$

$$\dot{Q}_{loss} / \dot{m} = \underline{h_{o,in} - h_{o,exit}}$$

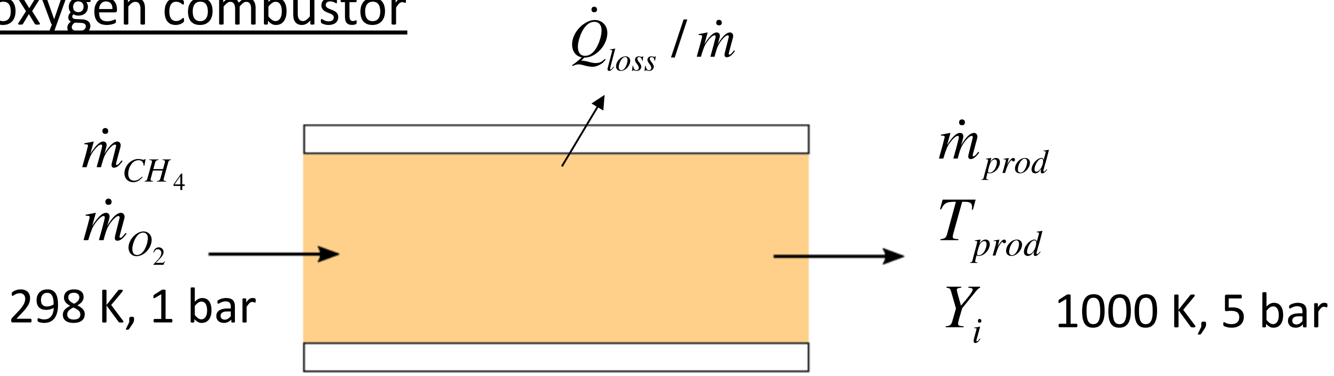
$$\frac{\dot{Q}_{loss}}{\dot{m}} = h_{o,reactants} - h_{o,products}$$

assume we know molar properties, so use $h = \bar{h} / MW$

$$= \frac{1}{MW_r} \sum_{\text{reactants}} \chi_i \left[\underbrace{\overset{\text{enthalpy}}{\left(\bar{h}_{T_{or}} - \bar{h}_{T_{ref}} \right)_i}} + \underbrace{\Delta \bar{h}^o_{f,T_{ref},i}} \right] - \frac{1}{MW_p} \sum_{\text{products}} \chi_i \left[\left(\bar{h}_{T_{op}} - \bar{h}_{T_{ref}} \right)_i + \Delta \bar{h}^o_{f,T_{ref},i} \right]$$

Example

Case of a methane-oxygen combustor



need to know composition of reactants and products

$$\frac{\dot{m}_{O_2}}{\dot{m}_{CH_4}} = \frac{5}{1} \Rightarrow \frac{n_{O_2}}{n_{CH_4}} = \frac{2.5}{1}$$

stoichiometric reaction:

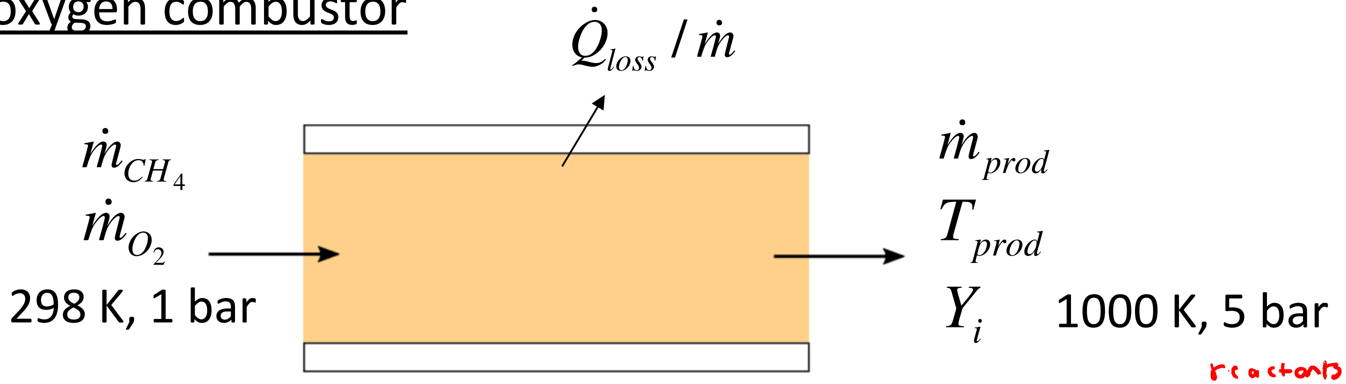
$$CH_4 + \underline{\ 2\ }\, O_2 \rightarrow \underline{\ 2\ }\, H_2O + \underline{\ 1\ }\, CO_2$$

H:	4		4	
C:	1			1
O:		4	2	2

$$4n^r_{CH_4} = 2n_{H_2O}$$
$$n^r_{CH_4} = n_{CO_2}$$
$$2n^r_{O_2} = n_{H_2O} + 2n_{CO_2} + 2n_{O_2}$$

Example

Case of a methane-oxygen combustor



but we already saw that $\frac{\dot{m}_{O_2}}{\dot{m}_{CH_4}} = \frac{5}{1} \Rightarrow \frac{n_{O_2}}{n_{CH_4}} = \frac{2.5}{1}$

reactants

$CH_4 = 2/7$

$O_2 = 5/7$

products

$\frac{4}{7}$ H_2O

$\frac{2}{7}$ CO_2

$\frac{1}{7}$ O_2

this means that more oxygen is present than needed, and does not react, i.e.:

$$\boxed{CH_4 + 2.5O_2 \rightarrow 2H_2O + 1CO_2 + \underline{0.5O_2}}$$

unreacted O_2

$$\underline{2CH_4 + 5O_2 \rightarrow 4H_2O + 2CO_2 + O_2}$$

$\chi_{CH_4,r} = 1/3.5$

$\chi_{O_2,r} = 2.5/3.5$

$\chi_{H_2O,p} = 2/3.5$

$\chi_{CO_2,p} = 1/3.5$

$\chi_{O_2,p} = 0.5/3.5$

compare to stoichiometric reaction:

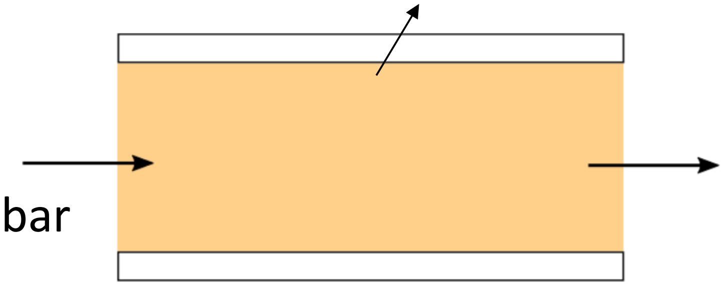
$$\underline{CH_4 + 2O_2 \rightarrow 2H_2O + 1CO_2}$$

Example

Georgia Tech

Case of a methane-oxygen combustor

$$\boxed{CH_4 + 2.5O_2 \rightarrow 2H_2O + 1CO_2 + 0.5O_2}$$



$\dot{Q}_{loss} / \dot{m}$

$\dot{m}_{CH_4}$

$\dot{m}_{O_2}$

298 K, 1 bar

$\dot{m}_{prod}$

T_{prod}

Y_i 1000 K, 5 bar

$$\dot{Q}_{loss} / \dot{m} = \frac{1}{MW_r} \sum_{reactants} \chi_i \left[\left(\bar{h}_{T_{or}} - \bar{h}_{T_{ref}} \right)_i + \Delta \bar{h}^o_{f,T_{ref},i} \right] - \frac{1}{MW_p} \sum_{products} \chi_i \left[\left(\bar{h}_{T_{op}} - \bar{h}_{T_{ref}} \right)_i + \Delta \bar{h}^o_{f,T_{ref},i} \right]$$

χ_i = mole fraction

CH4 **O2** (16+16)

$$MW_r = \sum_r \chi_i MW_i = \tfrac{2}{7} 16 + \tfrac{5}{7} 32 = 27.43 \tfrac{kg}{kmol_{mix}}$$

C=12+4(1)

H20 **CO2** **O2**

$$MW_p = \tfrac{4}{7} 18 + \tfrac{2}{7} 44 + \tfrac{1}{7} 32 = 27.43 \tfrac{kg}{kmol_{mix}}$$

16+2(1)

not typical for both MW's to be same

	h_{1000K}-h_{298K} (kJ/mol)	**$\Delta h_{f,298K}$ (kJ/mol)**
CH_4	38.179	-74.87
O_2	22.703	---
H_2O	26.000	-241.83
CO_2	33.397	-393.52

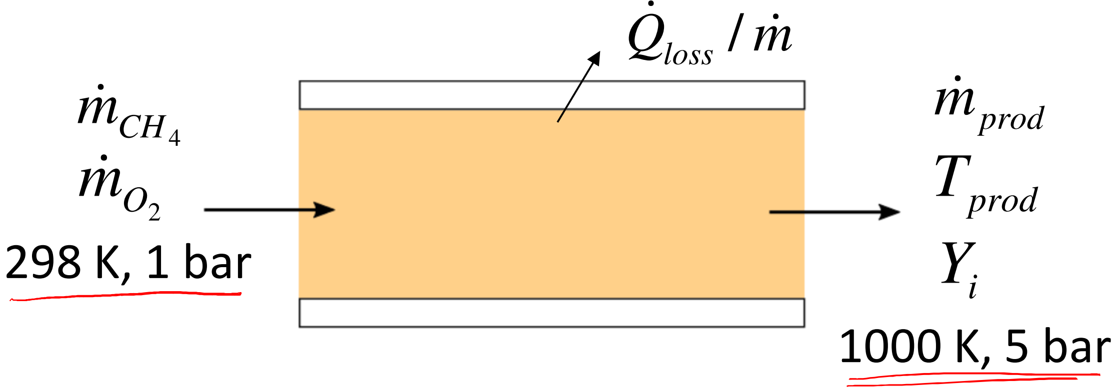
from janaf.nist.gov, with T_{ref}=298K

enthalpy of formation zero for O_2

Example

Case of a methane-oxygen combustor

$$\boxed{CH_4 + 2.5O_2 \rightarrow 2H_2O + 1CO_2 + 0.5O_2}$$



	h_{1000K}-h_{298K} (kJ/mol)	$\Delta h_{f,298K}$ (kJ/mol)
CH_4	38.179	-74.87 *
O_2	22.703	---
H_2O	* 26.000	-241.83 *
CO_2	* 33.397	-393.52

$$\dot{Q}_{loss}/\dot{m} = \frac{1}{MW_r}\sum_{\text{reactants}}\chi_i\left[\left(\bar{h}_{T_{or}}-\bar{h}_{T_{ref}}\right)_i+\Delta\bar{h}^o_{f,T_{ref},i}\right] - \frac{1}{MW_p}\sum_{\text{products}}\chi_i\left[\left(\bar{h}_{T_{op}}-\bar{h}_{T_{ref}}\right)_i+\Delta\bar{h}^o_{f,T_{ref},i}\right]$$

χ_i = mole fraction

CH4 O2 H20 CO2

$$= \frac{1}{27.43\frac{kg}{kmol}}\left\{\frac{2}{7}(0-74.87)+\frac{5}{7}(0+0)\right\}\frac{kJ}{mol}\frac{10^3\,mol}{kmol} - \frac{1}{27.43\frac{kg}{kmol}}\left\{\begin{aligned}&\frac{4}{7}(26-241.83)\\&+\frac{2}{7}(33.397-393.52)\\&+\frac{1}{7}(22.703+0)\end{aligned}\right\}\frac{kJ}{mol}\frac{10^3\,mol}{kmol}$$

O2

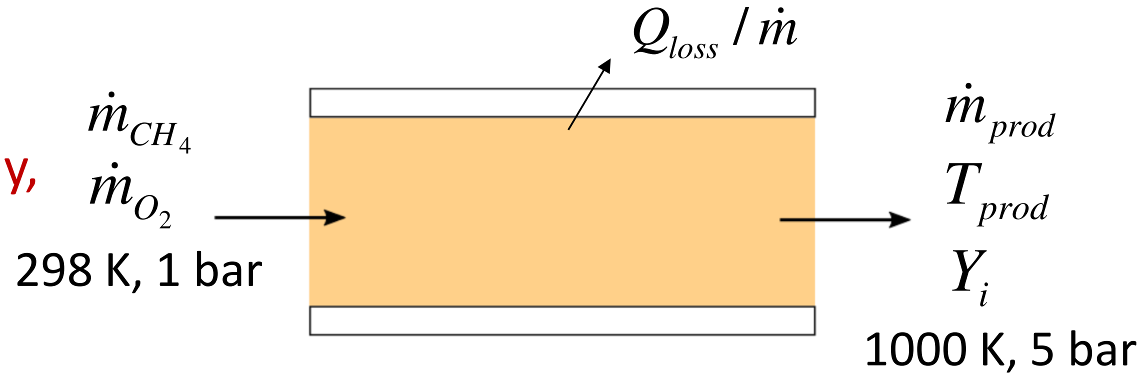
mole ratio

$$\boxed{\frac{\dot{Q}_{loss}}{\dot{m}} = 7.35\frac{MJ}{kg}} \text{ or } \frac{MW}{kg/s}$$

Example

Case of a methane-oxygen combustor

alternatively, using *cp*



Product	**c_p (J/molK)**		
	298 K	**1000 K**	**$c_{p,avg}$** *
H_2O	33.590	41.268	37.43
CO_2	37.129	54.308	45.72
O_2	29.376	34.870	32.13

from janaf.nist.gov

$$\dot{Q}_{loss}/\dot{m} = \frac{1}{MW_r}\sum_{\text{reactants}}\chi_i\left[\left(\bar{h}_{T_{or}}-\bar{h}_{T_{ref}}\right)_i+\Delta\bar{h}^o_{f,T_{ref},i}\right] - \frac{1}{MW_p}\sum_{\text{products}}\chi_i\left[\left(\bar{h}_{T_{op}}-\bar{h}_{T_{ref}}\right)_i+\Delta\bar{h}^o_{f,T_{ref},i}\right]$$

CH4 O2 H20 $c_p\Delta T$ h_f CO2 O2

$$= \frac{1}{27.43\,\frac{kg}{kmol}}\left\{\tfrac{2}{7}(0-74.87)+\tfrac{5}{7}(0+0)\right\}\frac{kJ}{mol}\,\frac{10^3\,mol}{kmol} - \frac{1}{27.43\,\frac{kg}{kmol}}\underbrace{\left\{\begin{array}{l}\tfrac{4}{7}(0.03743\times702-241.83)\\+\tfrac{2}{7}(0.04572\times702-393.52)\\+\tfrac{1}{7}(0.03213\times702)\end{array}\right\}}_{c_p\Delta T}\frac{kJ}{mol}\,\frac{10^3\,mol}{kmol}$$

$$\boxed{\frac{\dot{Q}_{loss}}{\dot{m}} = 7.35\frac{MJ}{kg}}$$

Analyzing the product composition

- in simplest cases:
  - combustion products known, from given reactants

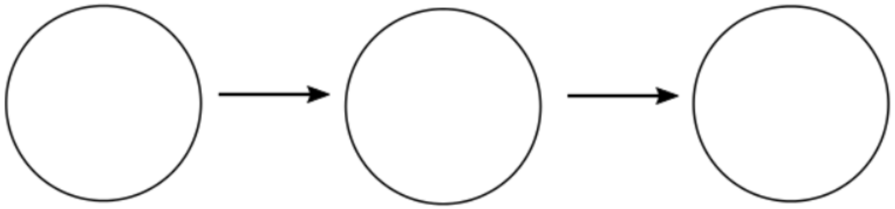
- in more complex, realistic situations (e.g. most fuel combustion cases)
  - multiple species in products: e.g. H2O, CO2, N2, O2, H2, CO..., etc.
  - more than one phase: e.g. soot

  Q. how much of each species is present?

- we can determine this if the products are in (quasi)equilibrium

System equilibrium

- start with an isolated system (or fixed energy *E* and volume *V*)
  - if we start out with initial non-equilibrium conditions, there will be a progression towards equilibrium



$\underline{T_1, \chi_{i\,1}}, \ldots$ $\quad T_2, \chi_{i\,2}, \ldots$ $\quad \underline{T_{eq}, \chi_{i\,eq}, \ldots}$

2nd Law of Thermodynamics

$$\underline{dS} = \underbrace{\cancel{\delta Q / T}}_{0} + \underbrace{\delta S_{pr}}_{\text{entropy produced}}$$

- entropy *S* will increase until we reach the equilibrium state with no more production of entropy, i.e. *S* is maximized

Equilibrium for fixed (T, p)

Q. what is the equilibrium composition for a known *T* and *p*?

2nd law

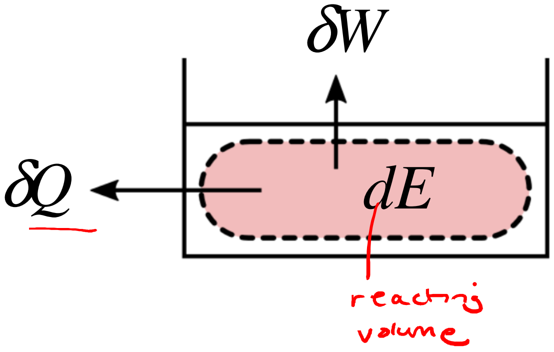
$$dS = -\delta Q/T + \delta S_{pr}$$

$$\delta Q = T\delta S_{pr} - TdS$$

entropy produced

1st law

$\delta W = pdV$



* $$dE = \delta Q_{in} - \delta W_{out}$$

$$dE = -\delta Q - \delta W$$

* $$dE + pdV + \delta Q = 0$$

combining 1st and 2nd laws,

$$dE + pdV - TdS = -T\delta S_{pr}$$

$$dE + \left(pdV + Vdp\right) - \left(TdS + SdT\right) = -T\delta S_{pr}$$

$$dE + d\left(pV\right) - d\left(TS\right) = -T\delta S_{pr}$$

$$dH - d\left(TS\right) = -T\delta S_{pr} \le 0$$

$d(pV) = dpV + dVp$

Gibbs Free Energy

$$G \equiv H - TS$$

$\Rightarrow dG \le 0$ G_{min}(T,p) at equilibrium

Equilibrium for fixed (T, p)

- so we can find what composition (χ_i) produces the minimum *G* for a given *T* and *p*

  requires computation

- alternative: analytical treatment for ideal gases

1. start by creating set of stoichiometric reactions (possible chemical "states")
2. use **Equilibrium "Constants"** (K_p) to find composition

RHS = products

LHS = reactants

p_j : partial pressure (products)

p_i : partial pressures (reactants)

p^o : ref. pressure (1 bar or 1 atm)

$$\frac{\prod_{j,RHS}\left(p_j/p^o\right)^{\nu_j}}{\prod_{i,LHS}\left(p_i/p^o\right)^{\nu_i}} = K_p(T)$$

reactants

Understanding the equilibrium constant

- Consider a mixture containing O_2, H_2O and OH at given *T* and *p*

Q. find the relationship between the mole fractions of each of these species at the given *T* and *p*

<u>assumptions</u>: ideal gases *

$$\boxed{\frac{\prod_{j,RHS}\left(p_j/p^o\right)^{\nu_j}}{\prod_{i,LHS}\left(p_i/p^o\right)^{\nu_i}} = K_p(T)}$$

1. stoichiometric reaction $$H_2O + \tfrac{1}{2}O_2 \leftrightarrow 2OH$$

one possible state
no OH

another state
all OH

prod.

1. equilibrium constant

react

$$\frac{\left(p_{OH}/p^o\right)^2}{\left(p_{H_2O}/p^o\right)^1\left(p_{O_2}/p^o\right)^{1/2}} = K_p$$

$$p_i = p\chi_i$$

$$\Downarrow$$

Po

$$\frac{\left(p\chi_{OH}\right)^2}{\left(p\chi_{H_2O}\right)^1\left(p\chi_{O_2}\right)^{1/2}} = \left(p^o\right)^{2-1-\frac{1}{2}} K_p$$

$$\chi_{OH}^2 = \chi_{H_2O}\chi_{O_2}^{1/2}\left(\frac{p^o}{p}\right)^{\frac{1}{2}} K_p(T) \Leftarrow$$