
Jet and Rocket Propulsion

AE4451

LECTURE 8

Overview

what we saw last time:

- chemical equilibrium thermodynamics
 - energy conservation accounting for chemical energy
 - stoichiometric reaction
 - use of reference table values (c_p , h_f , Δh over temperature range)
 - notion of the equilibrium constant

today:

- equilibrium constant
- deducing product composition for non-stoichiometric reaction

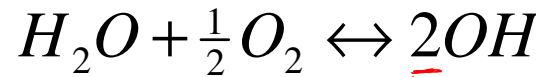
Understanding the equilibrium constant

- 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

assumptions: ideal gases

1. stoichiometric reaction



one possible state
no OH

another state
all OH

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

1. equilibrium constant

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

p° : ref. pressure (1 bar or 1 atm)

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

$$p_i = p \chi_i$$



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

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

assumptions: ideal gases

for same T , less OH at high p ; high p favors fewer moles

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

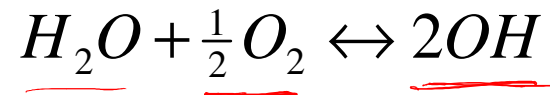
with $p^o = 1$ (atm or bar)

$$\chi_{OH}^2 = \chi_{H_2O} \chi_{O_2}^{1/2} p^{-1/2} K_p(T)$$

in other words, K_p gives us an idea of the product to reactant concentration

Understanding the equilibrium constant

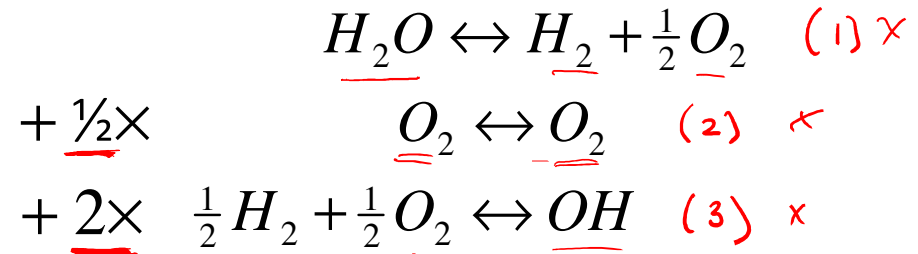
- Consider our mixture containing O_2 , H_2O and OH at given T and p



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

- we can write this as the sum of formation reactions:

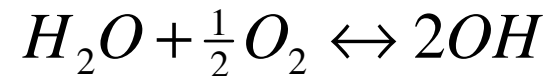
i.e. writing each compound as formed directly from its elements



$$\begin{aligned} K_p &= \frac{(p_{OH}/p^\circ)^2}{(p_{H_2O}/p^\circ)(p_{O_2}/p^\circ)^{1/2}} = \left\{ \frac{(p_{O_2}/p^\circ)^{1/2} (p_{H_2}/p^\circ)}{(p_{H_2O}/p^\circ)} \times \left[\frac{(p_{O_2}/p^\circ)}{(p_{O_2}/p^\circ)} \right]^{1/2} \times \left[\frac{(p_{OH}/p^\circ)}{(p_{H_2}/p^\circ)^{1/2} (p_{O_2}/p^\circ)^{1/2}} \right]^2 \right\} \\ &\Rightarrow K_p = \frac{1}{K_{p,f,H_2O}} \times \frac{1}{K_{p,f,O_2}^{1/2}} \times K_{p,f,OH}^2 \end{aligned}$$

Understanding the equilibrium constant

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



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

$$K_p = \frac{1}{K_{p,f,H_2O}} \times \frac{1}{K_{p,f,O_2}^{1/2}} \times \underbrace{K_{p,f,OH}^2}_{\text{formation constant}}$$

more generally, we obtain

$$K_p(T) = \frac{\prod_{j,RHS} K_{p,f}^{\nu_j}(T)}{\prod_{i,LHS} K_{p,f}^{\nu_i}(T)}$$

"formation constant"

$K_{p,f}(T)$ (also written K_f) is a thermodynamic property for a given species – e.g., available at janaf.nist.gov

Determining the product state

So far, some assumptions made for the problems we have solved

- “final” composition was known and we found the final temperature
- temperature (and pressure) known and we found composition (assuming chemical equilibrium)

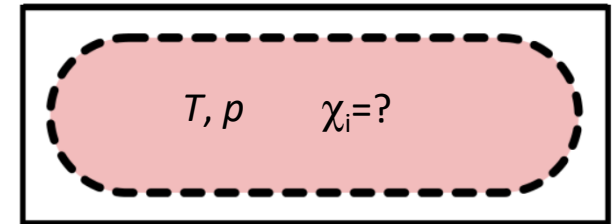
In general we don't know final T or composition

- requires solving both energy equations (i.e., using Δh_f 's to find T) AND the entropic equation (e.g, K_p to find χ_i)
- typically an iterative process
 - guess composition and find T
 - use new T to find composition
 - use new composition to find new T
 - iterate until convergence
- incorporated into chemical equilibrium software
 - NASA CEA, Gaseq, ...

Determining the product state

- Consider a case of "fuel-rich" combustion

CH₄-O₂ rocket combustion chamber burning with excess fuel (fuel-to-oxidizer ratio greater than stoichiometric amount, e.g, 1.9×)



Q. What is the equilibrium product composition (mole fractions) with known T and p (e.g., 2800 K, 100 atm)?

assumptions

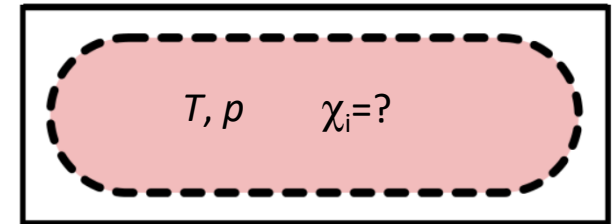
- ideal gases
- rich products primarily CO₂, H₂O, CO and H₂

Determining the product state

- unknowns:

mole ratios χ_{CO_2} χ_{CO} χ_{H_2} χ_{H_2O}

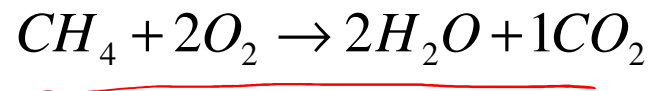
- we need 4 equations



- start with atom balances:

atoms for reactants = # atoms for products

recall from previous lecture:

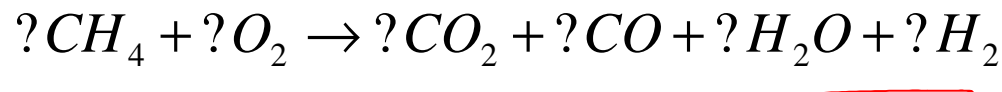


stoichiometric: AFR = 2 : 1



air-to-fuel ratio (AFR) > stoich.
= "lean mixture" 2.5 : 1

this problem:



air-to-fuel ratio (AFR) < stoich.
= "rich mixture"

Determining the product state

- atom balances

Reactants Products

n = number of atoms

$$\text{H: } 4n_{CH_4}^r = 2n_{H_2O} + 2n_{H_2}$$

$$\text{C: } n_{CH_4}^r = n_{CO_2} + n_{CO}$$

$$\text{O: } 2n_{O_2}^r = n_{H_2O} + 2n_{CO_2} + n_{CO}$$

$$\frac{4n_{CH_4}^r}{n_{prod}} = \frac{2n_{H_2O} + 2n_{H_2}}{n_{prod}}$$

in terms of mole fractions

$$\text{H: } 4n_{CH_4}^r / n_{prod} = 2\chi_{H_2O} + 2\chi_{H_2}$$

$$\text{C: } n_{CH_4}^r / n_{prod} = \chi_{CO_2} + \chi_{CO}$$

$$\text{O: } 2n_{O_2}^r / n_{prod} = \chi_{H_2O} + 2\chi_{CO_2} + \chi_{CO}$$

removing n_{prod}

$$\text{H/C: } \frac{4n_{CH_4}^r}{n_{CH_4}^r} = \frac{2\chi_{H_2O} + 2\chi_{H_2}}{\chi_{CO_2} + \chi_{CO}} \quad (1)$$

$$\text{O/C: } \frac{2n_{O_2}^r}{n_{CH_4}^r} = \frac{\chi_{H_2O} + 2\chi_{CO_2} + \chi_{CO}}{\chi_{CO_2} + \chi_{CO}} \quad (2)$$

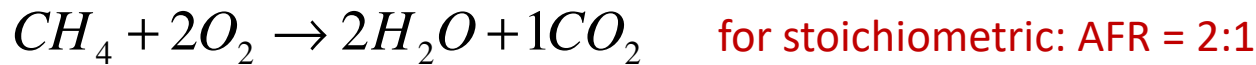
so two equations so far

Determining the product state

- applying mole fractions constraint

$$\underbrace{\chi_{H_2O} + \chi_{CO_2} + \chi_{CO} + \chi_{H_2}}_{\text{products}} = \sum_i \chi_i = 1 \quad (3)$$

- from problem statement



here, AFR is given as a multiple of stoichiometric ratio

$$\phi CH_4 + 2O_2 \quad \phi = 1.9 \quad \text{i.e.} \quad \frac{n_{O_2}^r}{n_{CH_4}^r} = \frac{2}{\phi}$$

- equilibrium constant: we need an expression

$$K_p(T) = \frac{\prod_{j,RHS} K_{p,f}^{v_j}(T)}{\prod_{i,LHS} K_{p,f}^{v_i}(T)}$$

k_p

$$K_p = \frac{(p\chi_{CO})(p\chi_{H_2O})}{(p\chi_{CO_2})(p\chi_{H_2})} = \frac{K_{p,f,CO} K_{p,f,H_2O}}{K_{p,f,CO_2} K_{p,f,H_2}} \quad (4)$$

i.e. mole ratios in terms of formation constants

Determining the product state

- so four equations for four unknowns

$$4 = \frac{2\chi_{H_2O} + 2\chi_{H_2}}{\chi_{CO_2} + \chi_{CO}} \quad (1) \qquad 1 = \chi_{H_2O} + \chi_{CO} + \chi_{H_2} \quad (3)$$

$$\frac{4}{\phi} = \frac{\chi_{H_2O} + 2\chi_{CO_2} + \chi_{CO}}{\chi_{CO_2} + \chi_{CO}} \quad (2) \qquad \frac{\chi_{CO}\chi_{H_2O}}{\chi_{CO_2}\chi_{H_2}} = \frac{K_{p,f,CO}K_{p,f,H_2O}}{K_{p,f,CO_2}K_{p,f,H_2}} \quad (4)$$

why?
 $CO_2 + H_2 \rightarrow CO + H_2O$
 products of our process;
 allows us to write out mole fractions in terms of known K_p 's
 ?

at 2800 K

	CO	H ₂ O	CO ₂
$K_{p,f}$	$3.624 \times 10^6 \text{ atm}^{-1/2}$	$45.8 \text{ atm}^{-1/2}$	$2.423 \times 10^7 \text{ atm}^{-1}$

we will find:

	CO	H ₂ O	CO ₂	H ₂
χ	29.22%	32.73%	4.11%	33.94%

Thermodynamic cycle analysis

- So far, we've been able to study different scenarios
 - non-reacting gases and flows and their thermodynamics
 - reactants and their compositions under different conditions
- we can use thermodynamics to study of systems that manipulate energy
 - heat engines: thermal energy conversion to work
 - thermal transfer systems: refrigeration, heat pumps
- these devices typically employ a working substance/fluid that goes through a (repeating) process

"thermodynamic cycle"

closed

same working fluid continuously
circulates through cycle

(steam power plant, refrigeration,...)

open

fluid enters and leaves device, but
new fluid (at same initial condition)
keeps replacing exhausted fluid
(jet engine, rocket, car engine,...)

Ideal cycles and state diagrams

Many real devices will be analyzed with **ideal cycle**:

1. assume ideal fluid, e.g., thermally, calorically perfect gas
2. simplify processes, e.g., combustor replaced by non-reacting heat exchanger
3. open system \rightarrow closed system, e.g., interaction with surroundings replaced with heat exchanger
4. assume reversibility, i.e., all components internally reversible

State diagrams are particularly helpful for visualizing cycle processes

