

Conditions for Equilibrium

- For **isolated system** (fixed mass, no energy exchange with environment)
 $\Rightarrow E, V$ constant, we know(?)

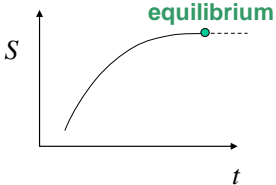
$$dS \geq 0$$

- In terms of the Gibbs Eq'n. (which holds if IN equil.)

$$TdS = dE + pdV$$

$$TdS \geq 0 \Rightarrow TdS - dE - pdV \geq 0$$

0 if isolated



More general: 1st/2nd Law

$$dE + \delta W - \delta Q = 0$$

$$dE + pdV - TdS + T\delta S_{prod} = 0$$

$$TdS - dE - pdV \geq 0$$

Equilibrium Condition for Fixed T, p

- We don't usually work with isolated systems
 – more common to ask, what is an equilibrium composition at a given T and p (for example, constant T, p process)

$$TdS - dE - pdV \geq 0$$

$$dT, dp = 0 \quad (TdS + SdT) - dE - (pdV + Vdp) \geq 0$$

$$d(TS) - dE - d(pV) \geq 0$$

$$d(TS) - dH \geq 0$$

$$G \equiv H - TS$$

Gibb's Free Energy

$$dG \leq 0$$

Equilibrium condition for given (T, p) is **MINIMUM G**

Finding Minimum G

- For a mixture of species, we have

$$G = \sum n_i \bar{g}_i$$

$$G(T, p) = \sum n_i \bar{g}_i(T, p_i)$$

- Solution method #1** ← *partial pressure for gas*
 - use minimization techniques to find n_i that give minimum mixture G (for given set of species)
 - e.g., using method of Lagrange Multipliers
 - “best” (fast, robust) equilibrium software use this approach
 - hard to do “by hand”

Minimizing G – K_p Approach

- Solution Method #2**

- break up g_i $\bar{g}_i(T, p_i) = \bar{h}_i(T) - T\bar{s}_i(T, p_i)$
- but state relation

$$d\bar{s} = \frac{d\bar{h}}{T} - \frac{\bar{v}}{T} dp = \frac{d\bar{h}}{T} - \bar{R} \frac{dp}{p} \quad \text{Perf. Gas}$$

T and p dep. separable

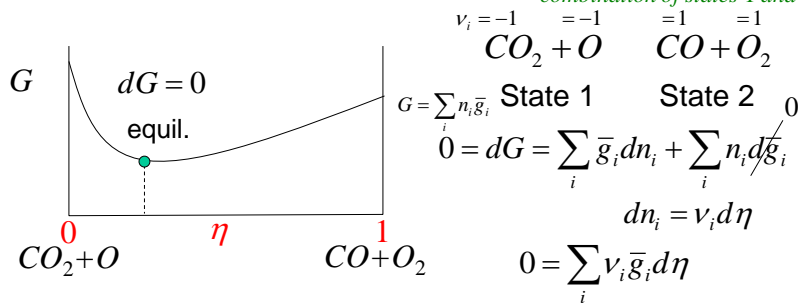
$$s_i = s_i^o(T) - R \ln \frac{p_i}{p^o}$$

$$\bar{g}_i(T, p_i) = \bar{h}_i - T\bar{s}_i^o + \bar{R}T \ln \frac{p_i}{p^o} = \bar{g}_i^o(T) + \bar{R}T \ln \left(\frac{p_i}{p^o} \right)$$

$$G = \sum n_i \left[\bar{g}_i^o(T) + \bar{R}T \ln \left(\frac{p_i}{p^o} \right) \right]$$

Equilibrium Constant Method

- Consider mixture of CO_2 , CO , O_2 and O at known T and p
- To find the composition that produces the minimum Gibbs free energy, we can imagine 2 possible "composition states" *any composition can be made from combination of states 1 and 2*



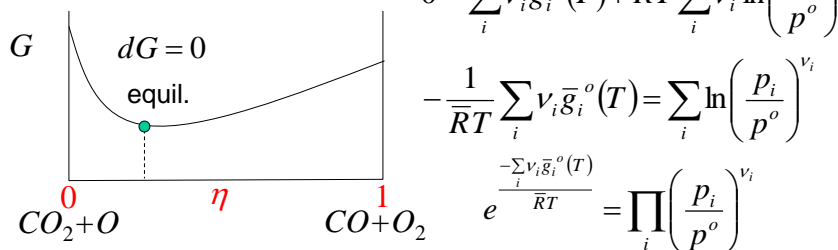
Chemical Equilibrium-6
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AE6450 Rocket Propulsion

Equilibrium Constant Method

- From previous result

– but $d\eta$ can't be zero



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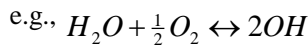
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Equilibrium Constant

- Defining the Gibbs free energy of the “reaction”

$$\Delta G_R^o \equiv \sum_i \nu_i \bar{g}_i^o(T) \quad R \leftrightarrow P$$

– we then have



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

$$e^{-\Delta G_R^o(T)/RT} = \prod_i \left(\frac{p_i}{p^o} \right)^{\nu_i}$$

$\equiv K_p$ Equilibrium Constant

- K_p is function of temperature only
 - essentially thermodynamic property of a (chemical) system
 - often drop p^o (usually 1 atm or bar)
- $$K_p = \frac{p_{OH}^2}{p_{H_2O} p_{O_2}^{1/2}}$$

Van't Hoff's Relation

- Taking derivative of K_p with T can show

$$\frac{d}{dT} (\ln K_p) = \frac{1}{RT^2} \Delta H_R^o$$

– where ΔH_R^o is the “heat of the reaction” (enthalpy difference between the RHS and LHS of the “reaction” at the given T)

- K_p increases with T for endothermic rxns. (chemical energy of RHS > LHS)
- K_p decreases with T for exothermic rxns.

Calculating K_p

- Recall $K_p = e^{-\Delta G_R^o(T)/\bar{R}T}$

$$\Delta G_R^o \equiv \sum_i \nu_i \bar{g}_i^o(T) \quad \bar{g}_i^o(T) = \bar{h}_i(T) - T \bar{s}_i(T, p^o)$$

- so just need to know thermodynamic properties of each species

- Alternate approach

- since any reaction can be made by summing up a set of formation reactions, can show $\log K_{p_f,i}$

$$K_p = \prod_i (K_{p_f,i})^{\nu_i}$$

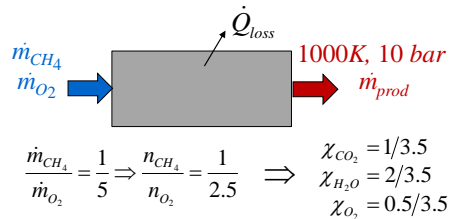
formation K_p for each species also available

$$K_{p_f,element} = ?$$

T/K	C_p^o	$\int_0^T C_p^o dT$	$\int_0^T C_p^o dT/T$	$H^o - H^o(T_0)$	$\Delta_f H^o$	$\Delta_f G^o$	$\log K_f$
0	0	0	INFINITE	-9.364	-393.151	-393.151	INFINITE
100	29.208	179.009	243.568	-6.456	-393.208	-393.683	205.639
200	32.359	199.975	217.046	-3.814	-393.404	-394.085	102.924
298.15	37.129	213.795	213.795	0	-393.512	-394.389	69.095
300	37.221	214.025	213.795	0.069	-393.523	-394.394	68.670
400	41.325	223.314	215.397	4.003	-393.583	-394.675	51.539
500	44.627	234.901	216.390	8.305	-393.666	-394.929	41.259
600	47.221	243.283	217.772	12.907	-393.803	-395.182	34.404
700	49.564	250.750	218.866	17.254	-393.983	-395.398	29.505
800	51.718	257.404	219.686	21.188	-394.188	-395.586	25.829

Example: Previous Rocket Problem

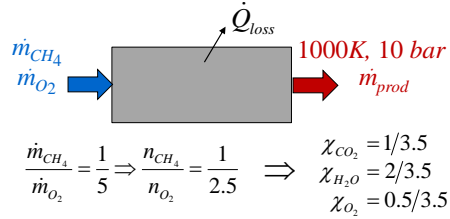
- Before we assumed products only $\text{CO}_2, \text{H}_2\text{O}, \text{O}_2$ and found composition from atom balances



- Was this assumption poor?
 - e.g., how much O, OH, H_2 ,... might be present?
- To find out, we can
 - solve full equilibrium composition problem
 - or **assume we were close and check**

Example: Previous Rocket Problem

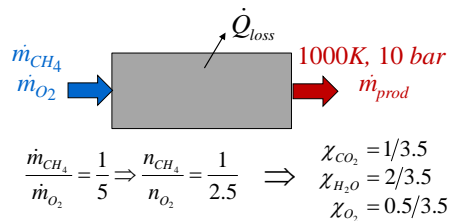
- How can we estimate how much OH if we say we know how much of the major products?



- consider following “thermodynamic state relation”

Example: Previous Rocket Problem

- How can we estimate how much OH if we say we know how much of the major products?



$$\chi_{OH}^2 = \frac{K_{p_f,OH}^2}{K_{p_f,H_2O} K_{p_f,O_2}^{1/2}} P^{-1/2} \chi_{H_2O} \chi_{O_2}^{1/2}$$

from kinetics.nist.gov/janaf/

$$K_{p_f,OH,1000K} = 10^{-1.222}$$

$$K_{p_f,H_2O,1000K} = 10^{10.060}$$

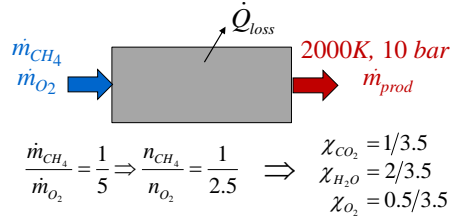
$$\chi_{OH} \approx 1.5 \times 10^{-7}$$

$$\chi_{CO} \cdot \chi_{H_2} \cdot \chi_O \approx O(10^{-11})$$

So would hardly change original χ_{H_2O} , χ_{CO_2} , χ_{O_2} values

Example: Previous Rocket Problem

- What if exit temp. increased to 2000K?



$$K_{p_f, OH, 2000K} = 10^{-0.240}$$

$$K_{p_f, H_2O, 2000K} = 10^{3.54}$$

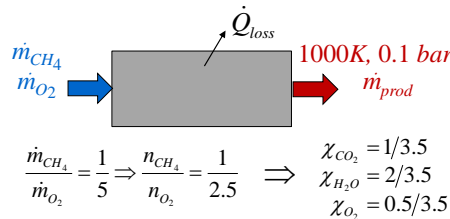
$$\Rightarrow \chi_{OH}(2000K) \approx 0.0025 \quad 0.25\%$$

$$\chi_{CO}, \chi_{H_2}, \chi_O \approx O(10^{-4})$$

Raising temperature **increases OH** and other minor species! Why?

Example: Previous Rocket Problem

- What if exit pressure decreased to 0.1 bar (but original T)?



$$\chi_{OH}^2 = \frac{K_{p_f, OH}^2}{K_{p_f, H_2O} K_{p_f, O_2}^{1/2}} p^{-1/2} \chi_{H_2O} \chi_{O_2}^{1/2}$$

$$\chi_{OH}(0.1bar) \approx 3.2(0.15 ppm) = 0.5 ppm$$

Lowering pressure **increases OH!** Why?

Full Problem: CH₄/O₂ Combustor

• **Given:**

- Gaseous methane and oxygen entering **adiabatic** combustor at 298 K, 10 bar
- Mass flowrate ratio of oxygen is 3× that for methane



• **Find:**

- both exit temperature AND composition

Full Problem: CH₄/O₂ Combustor

• **Solution:**

$$\frac{\dot{m}_{CH_4}}{\dot{m}_{O_2}} = \frac{1}{3} \Rightarrow \frac{n_{CH_4}}{n_{O_2}} = \frac{1}{1.5}$$



- Energy Equation (adiabatic, no work)

$$\frac{1}{MW_{\text{Reactants}}} \sum_{\text{Reactants}} \chi_i \left[(\bar{h}_T - \bar{h}_{T_{ref}})_i + \Delta \bar{h}_{f,T_{ref},i}^o \right] = \frac{1}{MW_{\text{Products}}} \sum_{\text{Products}} \chi_i \left[(\bar{h}_T - \bar{h}_{T_{ref}})_i + \Delta \bar{h}_{f,T_{ref},i}^o \right]$$

For $T_{ref} = 298K$

$$\frac{1}{MW_{\text{Reactants}}} \sum_{\text{Reactants}} \chi_i \left[(\bar{h}_T - \bar{h}_{298K})_i + \Delta \bar{h}_{f,298K,i}^o \right] = \frac{1}{MW_{\text{Products}}} \sum_{\text{Products}} \chi_i \left[(\bar{h}_T - \bar{h}_{298K})_i + \Delta \bar{h}_{f,298K,i}^o \right] \quad (1) \quad T \text{ and } \chi_i \text{ unknown}$$

Full Problem: CH₄/O₂ Combustor

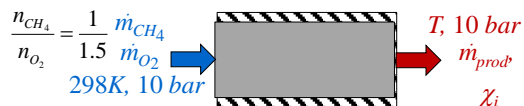
• **Solution:**



- recall stoichiometric mixture ratio is 1/2 CH₄:O₂
- now we have excess fuel (rich) reactant mixture, no excess O₂ and unburned fuel does not stay CH₄ (not at high temperatures)
 - rich products might include: H₂O, CO₂, CO, H₂, H, OH, O, ...
- need to find: T, χ_{H₂O}, χ_{CO₂}, χ_{CO}, χ_{H₂}, χ_H, χ_{OH}, χ_O
- using: energy conservation, atom balances, and K_p equations (2nd Law) **How many?**

Full Problem: CH₄/O₂ Combustor

• **Solution:**



- atom balances

$$\frac{n^C}{n^H} = \frac{1}{4}$$

$$\frac{n^C}{n^O} = \frac{1}{3}$$

$$\sum_{\text{products}} \chi_i = \chi_{H_2O} + \chi_{CO_2} + \chi_{CO} + \chi_{H_2} + \chi_H + \chi_{OH} + \chi_O$$

H₂O, CO₂, CO,
H₂, H, OH, O

Full Problem: CH₄/O₂ Combustor

• **Solution:**

– K_p eqns

- many choices; must include all and be independent

$$\frac{n_{CH_4}}{n_{O_2}} = \frac{1}{1.5} \frac{\dot{m}_{CH_4}}{\dot{m}_{O_2}}$$



$H_2O, CO_2, CO,$
 H_2, H, OH, O

8 eqn's, 8 unknowns \Rightarrow solve!!

Full Problem: CH₄/O₂ Combustor

• **Solution:**

– result

$$\frac{n_{CH_4}}{n_{O_2}} = \frac{1}{1.5} \frac{\dot{m}_{CH_4}}{\dot{m}_{O_2}}$$



$H_2O, CO_2, CO,$
 H_2, H, OH, O

T (K)	χ_{H_2O}	χ_{CO_2}	χ_{CO}	χ_{H_2}	χ_{OH}	χ_H	χ_O
3352	43.6%	9.58%	21.3%	12.3%	7.05%	4.60%	1.53%

None of these species are "negligible" at these conditions

0.1 bar

T (K)	χ_{H_2O}	χ_{CO_2}	χ_{CO}	χ_{H_2}	χ_{OH}	χ_H	χ_O
2796	38.0%	9.16%	20.2%	12.2%	7.93%	8.90%	3.57%

Primarily, water dissociated to make H and O