



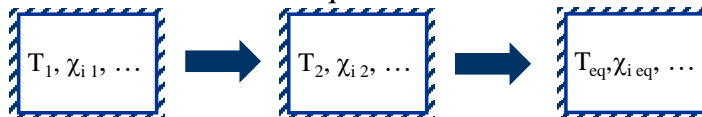
Determining Product Composition

- **Previously**
 - we assumed we knew combustion products
- **In general for hydrocarbon fuel burning with air**
 - many species can exist in products
 - H₂O, CO₂, N₂, O₂, H₂, CO, OH, C_xH_y, NO, soot, ...
 - **how much of each?**
- Can provide “simple” answer if we assume the products are in (or very close to being in) **chemical equilibrium**
- Not just useful for combustion – general approach for chemical reacting system

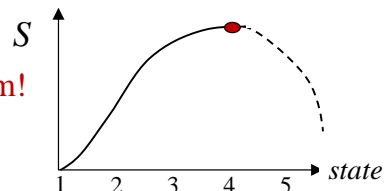


System Moving to Equilibrium

- Start with isolated system (or fixed E and V)
 - given initial *non-equilibrium* conditions, what will happen if we wait
 - will move towards equilibrium



- **2nd Law:** $dS = \delta Q/T + \delta S_{pr}$
 - S increases until no more production... **equilibrium!**
 - S is $S_{max}(E, V)$ at the **equilibrium state**

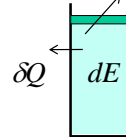




Equilibrium for Fixed (T, p)

- What if we want to know what is equilibrium composition for a known temperature & pressure $\delta W = pdV$
- Consider 2nd AND 1st Laws for CM

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



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

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

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

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

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

$$\Rightarrow dG \leq 0$$

Gibbs Free Energy

$$G \equiv H - TS$$

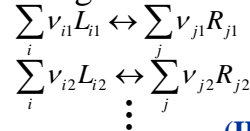
$G_{min}(T, p)$ at equilibrium



Equilibrium Chem. Composition

- So can find what composition (χ_i) produces the minimum G for a given T and p
 - intensive process; requires computer
- A simpler process that accomplishes same thing can be done analytically (by hand) for ideal gases

1. Start by creating set of stoichiometric reactions (possible chemical “states”)



(II.16)

2. Use **Equilibrium “Constants”** (K_p) to find composition

p_i : partial pressures

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

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

function of temp.



Example: OH in Wet Air

- Given:** Mixture containing O_2 , H_2O and OH at given T and p
- Find:** Relationship between the mole fractions of each of these species at the given T and p

T, p
 O_2, H_2O, OH

- Assume:** Ideal gases
- Analysis:**

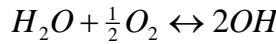
one possible state
no OH

another state
all OH

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

equil. is somewhere in-between

1) Write stoich. "reaction"



2) Equil. Constant

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

$$p_i = p\chi_i$$

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



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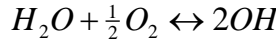
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equil. is somewhere in-between

1) Write stoich. "reaction"



2) Equil. Constant

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

*How does χ_{OH} depend on
pressure if we keep T constant?*

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

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

with $p^\circ = 1$ (atm or bar)



How to Find K_p Values

- Consider our example “reaction” $H_2O + \frac{1}{2}O_2 \leftrightarrow 2OH$
- We can write this as the sum of formation “reactions”
 - $H_2O \leftrightarrow H_2 + \frac{1}{2}O_2$
 - + $\frac{1}{2} \times O_2 \leftrightarrow O_2$
 - + $2 \times \frac{1}{2} H_2 + \frac{1}{2} O_2 \leftrightarrow OH$
- equivalently

$$K_p = \frac{(p_{OH}/p^\circ)^2}{(p_{H_2O}/p^\circ)(p_{O_2}/p^\circ)^{1/2}} = \left\{ \frac{(p_{O_2}/p^\circ)^{1/2} (p_{H_2}/p^\circ)}{(p_{H_2O}/p^\circ)} \times \left[\frac{(p_{O_2}/p^\circ)}{(p_{O_2}/p^\circ)} \right]^{1/2} \right.$$

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

- Generally (II.17)

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

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



Determining Product State

- So far**
 - first, we assumed we knew “final” composition and found final (post-reaction) temperature
 - second, we assumed we knew temperature (and pressure) and found composition (assuming chemical equilibrium)
- In general we don’t know final T or composition**
 - requires solving both energy equation (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, ...