

## ***Outline***

**USC**Viterbi  
School of Engineering

- Why do we need to invoke chemical equilibrium?
- Degrees Of Reaction Freedom (DORFs)
- Conservation of atoms
- Second Law of Thermodynamics for reactive systems
- Equilibrium constants
- Application of chemical equilibrium to hydrocarbon-air combustion
- Application of chemical equilibrium to compression /expansion processes

## Why do we need chemical equilibrium?

- (From Lecture 2) What if we assume more products, e.g.  
 $1\text{CH}_4 + 2(\text{O}_2 + 3.77\text{N}_2) \rightarrow ? \text{CO}_2 + ? \text{H}_2\text{O} + ? \text{N}_2 + ? \text{CO}$   
In this case how do we know the amount of CO vs. CO<sub>2</sub>?
- And if we assume only 3 products, how do we know that the “preferred” products are CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub> rather than (for example) CO, H<sub>2</sub>O<sub>2</sub> and N<sub>2</sub>O?
- Need **chemical equilibrium** to decide - use 2nd Law to determine the worst possible end state of the mixture

## Degrees of reaction freedom (DoRFs)

- If we have a reacting “soup” of 6 different types of molecules (N = 6), e.g., CO, O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub> and OH, can we specify changes in the amount of each molecule independently? No, we must conserve each type of atom (3 in this case)
- Conservation of
  - C atoms:  $n_{\text{CO}} + n_{\text{CO}_2} = \text{constant}$  ( $n_i = \text{number of moles of } i$ )
  - O atoms:  $n_{\text{CO}} + 2n_{\text{CO}_2} + 2n_{\text{O}_2} + n_{\text{H}_2\text{O}} + n_{\text{OH}} = \text{constant}$
  - H atoms:  $2n_{\text{H}_2\text{O}} + 2n_{\text{H}_2} + n_{\text{OH}} = \text{constant}$
- 3 equations, 6 unknown  $n_i \Rightarrow$  3 **degrees of reaction freedom (DoRFs)**
- **# of DoRFs = # of different molecules (N) - # of different elements**
- Each DoRF will result in the requirement for one equilibrium constraint

## Conservation of atoms

- Typically we apply conservation of atoms by requiring that the **ratios** of atoms are constant, *i.e.*, same in reactants and products

C atoms:  $n_{CO} + n_{CO_2} = \text{constant}$

O atoms:  $n_{CO} + 2n_{CO_2} + 2n_{O_2} + n_{H_2O} + n_{OH} = \text{constant}$

H atoms:  $2n_{H_2O} + 2n_{H_2} + n_{OH} = \text{constant}$

$$\frac{n_C}{n_O} = \frac{X_{CO} + X_{CO_2}}{X_{CO} + 2X_{CO_2} + 2X_{O_2} + X_{H_2O} + X_{OH}} = \text{constant}$$

$$\frac{n_C}{n_H} = \frac{X_{CO} + X_{CO_2}}{2X_{H_2O} + 2X_{H_2} + X_{OH}} = \text{constant}$$

- Specifying  $n_O/n_H$  also would be redundant, so the number of atom ratio constraints = # of types of atoms – 1

## Conservation of atoms

- But wait, this is only two constraint equations and we have 3 types of atoms – is something missing? Yes, we need sum of all mole fractions = 1, *e.g.*,

$$\sum_{i=1}^N X_i = 1 \Rightarrow X_{CO} + X_{CO_2} + X_{O_2} + X_{H_2O} + X_{OH} + X_{H_2} = 1$$

- What are these “constants?” Depends on initial mixture, *e.g.*, for a mixture of  $CH_4$  with  $O_2$  with  $CH_4:O_2 = 1:3$  we have  $1CH_4 + 3O_2$  thus  $n_C/n_O = 1/6$ ,  $n_C/n_H = 1/4$ , **regardless of what products are formed, because atoms must be conserved in any chemical reaction**

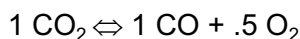
## 2nd law of thermo for reacting systems USC Viterbi School of Engineering

- Constraints for reacting system in a simple compressible substance (a substance with PdV work only)
  - First law:  $dE = \delta Q - \delta W = \delta Q - PdV$
  - Second law:  $dS \geq \delta Q/T$
  - Combine:  $TdS - dU - PdV \geq 0$  for any allowable change in the state of the system
  - For a system at fixed T and P (e.g. material in a piston-cylinder with fixed weight on top of piston, all placed in isothermal bath):  $d(TS-U-PV) \geq 0$ , or per unit mass  $d(Ts-u-Pv) \geq 0$
  - Define "Gibbs function"  $g \equiv h - Ts = u + Pv - Ts$
  - Thus for system at fixed T and P:  $d(-g) \geq 0$  or  $dg \leq 0$
  - Thus at equilibrium,  $dg = 0$  (g is minimum)
  - Similarly, for system at fixed U and V (e.g. insulated chamber of fixed volume):  $ds \geq 0$ , at equilibrium  $ds = 0$  (s is maximum)

AME 436 - Spring 2019 - Lecture 3 - Chemical Thermodynamics 2 7

## 2nd law of thermo for reacting systems USC Viterbi School of Engineering

- For a mixture of ideal gases with 1 DoRF that reacts according to  $v_A A + v_B B \Leftrightarrow v_C C + v_D D$ , e.g.



A = CO<sub>2</sub>, v<sub>A</sub> = 1, B = nothing, v<sub>B</sub> = 0, C = CO, v<sub>C</sub> = 1, D = O<sub>2</sub>, v<sub>D</sub> = 0.5

with  $dg = 0$ , "it can be shown"

$$\frac{X_C^{v_C} X_D^{v_D}}{X_A^{v_A} X_B^{v_B}} \left( \frac{P}{P_{ref}} \right)^{v_C + v_D - v_A - v_B} = \frac{K_C^{v_C} K_D^{v_D}}{K_A^{v_A} K_B^{v_B}}$$

$$X_i = \text{mole fraction of } i = \frac{n_i}{n_{total}} = \frac{n_i}{\sum_{i=1}^N n_i}; \text{ recall } \sum_{i=1}^N X_i = 1$$

Note  $n_{total}$  includes all species in the mixture, not just A, B, C, and D

$P$  = total pressure,  $P_{ref}$  = reference pressure = 1 atm

$K_i$  = equilibrium constant of  $i$  (from tables) = function of T only (not P)

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## Equilibrium constants

- Examples of tabulated data on K - (double-click table to open Excel spreadsheet with all data for CO, O, CO<sub>2</sub>, C, O<sub>2</sub>, H, OH, H<sub>2</sub>O, H<sub>2</sub>, N<sub>2</sub>, NO at 200K - 6000K)
- Note K = 1 at all T for elements in their standard state (e.g. O<sub>2</sub>)

CO  
Molecular weight = 28.01054 g/mole  
Δh<sub>f</sub><sup>o</sup> (kJ/mole) -110.541

T K	h-h 298 kJ/mole	Keq (no units)
200	-2.858	3.567E+25
298	0.000	1.190E+16
300	0.054	9.085E+15
400	2.975	1.360E+11
500	5.929	1.664E+08
600	8.941	1.854E+06
700	12.021	7.334E+04
800	15.175	6.416E+03
900	18.397	9.701E+02
1000	21.686	2.067E+02
1100	25.033	5.870E+01
1200	28.428	2.050E+01
1300	31.865	8.382E+00
1400	35.338	3.886E+00
1500	38.848	1.991E+00
1600	42.384	1.106E+00
1700	45.940	6.577E-01
1800	49.522	4.136E-01
1900	53.124	2.728E-01
2000	56.739	1.876E-01
2100	60.375	1.333E-01
2200	64.019	9.767E-02
2300	67.676	7.350E-02
2400	71.346	5.656E-02
2500	75.023	4.443E-02

O<sub>2</sub>  
Molecular weight = 31.99879 g/mole  
Δh<sub>f</sub><sup>o</sup> (kJ/mole) 0.000

T K	h-h 298 kJ/mole	Keq (no units)
200	-2.866	1.000E+00
298	0.000	1.000E+00
300	0.054	1.000E+00
400	3.029	1.000E+00
500	6.088	1.000E+00
600	9.247	1.000E+00
700	12.502	1.000E+00
800	15.841	1.000E+00
900	19.246	1.000E+00
1000	22.707	1.000E+00
1100	26.217	1.000E+00
1200	29.765	1.000E+00
1300	33.351	1.000E+00
1400	36.966	1.000E+00
1500	40.610	1.000E+00
1600	44.279	1.000E+00
1700	47.970	1.000E+00
1800	51.689	1.000E+00
1900	55.434	1.000E+00
2000	59.199	1.000E+00
2100	62.986	1.000E+00
2200	66.802	1.000E+00
2300	70.634	1.000E+00
2400	74.492	1.000E+00
2500	78.375	1.000E+00

CO<sub>2</sub>  
Molecular weight = 44.00995 g/mole  
Δh<sub>f</sub><sup>o</sup> (kJ/mole) -393.522

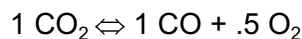
T K	h-h 298 kJ/mole	Keq (no units)
200	-3.414	8.148E+94
298	0.000	1.395E+61
300	0.067	5.248E+60
400	4.008	3.678E+43
500	8.314	1.764E+33
600	12.916	2.265E+26
700	17.761	2.662E+21
800	22.815	5.295E+17
900	28.041	7.065E+14
1000	33.405	3.439E+12
1100	38.894	4.454E+10
1200	44.484	1.190E+09
1300	50.158	5.548E+07
1400	55.907	4.013E+06
1500	61.714	4.119E+05
1600	67.580	5.622E+04
1700	73.492	9.700E+03
1800	79.442	2.037E+03
1900	85.429	5.043E+02
2000	91.450	1.437E+02
2100	97.500	4.612E+01
2200	103.575	1.644E+01
2300	109.671	6.406E+00
2400	115.788	2.702E+00
2500	121.926	1.222E+00

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9

## Chemical equilibrium - example

- For a mixture of CO, O<sub>2</sub> and CO<sub>2</sub> (and nothing else, 1 DoRF) at 10 atm and 2500K with C:O = 1:3, what are the mole fractions of CO, O<sub>2</sub>, CO<sub>2</sub>?



$$\frac{X_{\text{CO}}^1 X_{\text{O}_2}^{.5}}{X_{\text{CO}_2}^1} \left( \frac{10 \text{ atm}}{1 \text{ atm}} \right)^{1+.5-1} = \frac{K_{\text{CO}}^1 K_{\text{O}_2}^{.5}}{K_{\text{CO}_2}^1} = \frac{0.04443^1 1^{.5}}{1.222^1} = 0.0364 \quad (\text{chem. equilibrium})$$

$$X_{\text{CO}} + X_{\text{O}_2} + X_{\text{CO}_2} = 1 \quad (\text{sum of mole fractions} = 1)$$

$$\frac{n_{\text{C}}}{n_{\text{O}}} = \frac{X_{\text{CO}} + X_{\text{CO}_2}}{X_{\text{CO}} + 2X_{\text{O}_2} + 2X_{\text{CO}_2}} = \frac{1}{3} \quad (\text{conservation of atoms})$$

- 3 equations, 3 unknowns: X<sub>CO<sub>2</sub></sub> = 0.6495, X<sub>O<sub>2</sub></sub> = 0.3376, X<sub>CO</sub> = 0.0129
- At 10 atm, 1000K: X<sub>CO<sub>2</sub></sub> = .6667, X<sub>O<sub>2</sub></sub> = 0.3333, X<sub>CO</sub> = 2.19 x 10<sup>-11</sup>
- At 1 atm, 2500K: X<sub>CO<sub>2</sub></sub> = 0.6160, X<sub>O<sub>2</sub></sub> = 0.3460, X<sub>CO</sub> = 0.0380
- With N<sub>2</sub> addition, C:O:N = 1:3:6, 10 atm, 2500K: X<sub>CO<sub>2</sub></sub> = 0.2141, X<sub>O<sub>2</sub></sub> = 0.1143, X<sub>CO</sub> = 0.0073, X<sub>N<sub>2</sub></sub> = 0.6643 (X<sub>CO<sub>2</sub></sub>/X<sub>CO</sub> = 29.3 vs. 50.3 without N<sub>2</sub> dilution) (note still 1 DoRF in this case)
- Note high T, low P and dilution favor dissociation

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10

## Chemical equilibrium

- How do I know to write the equilibrium as



and not (for example)



For the first form

$$\frac{X_{\text{CO}}^1 X_{\text{O}_2}^{.5} \left( \frac{P}{P_{\text{ref}}} \right)^{1+.5-1}}{X_{\text{CO}_2}^1} = \frac{K_{\text{CO}}^1 K_{\text{O}_2}^{.5}}{K_{\text{CO}_2}^1} \Rightarrow \frac{X_{\text{CO}}^2 X_{\text{O}_2}^1 \left( \frac{P}{P_{\text{ref}}} \right)^{2+1-2}}{X_{\text{CO}_2}^2} = \frac{K_{\text{CO}}^2 K_{\text{O}_2}^1}{K_{\text{CO}_2}^2}$$

$$\Rightarrow \frac{X_{\text{CO}_2}^2}{X_{\text{CO}}^2 X_{\text{O}_2}^1 \left( \frac{P}{P_{\text{ref}}} \right)^{2-2-1}} = \frac{K_{\text{CO}_2}^2}{K_{\text{CO}}^2 K_{\text{O}_2}^1}$$

which is the appropriate expression of equilibrium for the 2nd form - so the answer is, **it doesn't matter as long as you're consistent**

## Chemical equilibrium - hydrocarbons

- Reactants:  $\text{C}_x\text{H}_y + r\text{O}_2 + s\text{N}_2$  (not necessarily stoichiometric)
- Assumed products:  $\text{CO}_2, \text{CO}, \text{O}_2, \text{O}, \text{H}_2\text{O}, \text{OH}, \text{H}, \text{H}_2, \text{N}_2, \text{NO}$
- How many equations?

- 10 species, 4 elements  $\Rightarrow$  6 DoRFs  $\Rightarrow$  6 equilibrium constraints

- 4 types of atoms  $\Rightarrow$  3 atom ratio constraints

- 1 Conservation of energy ( $h_{\text{reactants}} = h_{\text{products}}$ ) (constant pressure reaction) or  $u_{\text{reactants}} = u_{\text{products}}$  (constant volume reaction)

- 1 Sum of mole fractions = 1  $\sum_{i=1}^N X_i = 1$

- 1 Pressure = constant or (for const. vol.)

- 6 + 3 + 1 + 1 + 1 = 12 equations

$$\frac{P_{\text{products}}}{P_{\text{reactants}}} = \frac{\sum_{i=1}^{N(\text{products})} n_i T_{\text{products}}}{\sum_{i=1}^{N(\text{reactants})} n_i T_{\text{reactants}}}$$

- How many unknowns?

- 10 species  $\Rightarrow$  10 mole fractions ( $X_i$ )

- 1 Temperature

- 1 Pressure

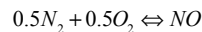
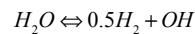
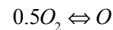
- 10 + 1 + 1 = 12 equations

- Equilibrium constraints - not a unique set, but for any set
  - Each species appear in at least one constraint
  - Each constraint must have exactly 1 DoRF
  - Note that the initial fuel molecule does not necessarily appear in the set of products! If the fuel is a large molecule, e.g.  $C_8H_{18}$ , its entropy is so low compared to other species that the probability of finding it in the equilibrium products is negligible!

- Example set (not unique)

$$CO_2 \Leftrightarrow CO + 0.5O_2 : \frac{X_{CO}^1 X_{O_2}^{0.5}}{X_{CO_2}^1} \left( \frac{P}{P_{ref}} \right)^{1+0.5-1} = \frac{[K_{CO}(T)]^1 [K_{O_2}(T)]^{0.5}}{[K_{CO_2}(T)]^1}$$

$$H_2O \Leftrightarrow H_2 + 0.5O_2 : \frac{X_{H_2}^1 X_{O_2}^{0.5}}{X_{H_2O}^1} \left( \frac{P}{P_{ref}} \right)^{1+0.5-1} = \frac{[K_{H_2}(T)]^1 [K_{O_2}(T)]^{0.5}}{[K_{H_2O}(T)]^1}$$



- Atom ratios

$$\frac{n_C}{n_O} = \frac{x}{2r} = \frac{X_{CO} + X_{CO_2}}{X_{CO} + 2X_{CO_2} + 2X_{O_2} + X_{H_2O} + X_{OH} + X_O + X_{NO}}$$

$$\frac{n_C}{n_H} = \frac{x}{y} = \frac{X_{CO} + X_{CO_2}}{2X_{H_2O} + 2X_{H_2} + X_{OH} + X_H}$$

$$\frac{n_C}{n_N} = \frac{x}{2s} = \frac{X_{CO} + X_{CO_2}}{2X_{N_2} + X_{NO}}$$

- Sum of all mole fractions = 1

$$\sum_{i=1}^N X_i = X_{CO} + X_{CO_2} + X_{O_2} + X_O + X_{H_2O} + X_{H_2} + X_{OH} + X_H + X_{N_2} + X_{NO} = 1$$

- Conservation of energy (constant P shown)

$$h_{\text{reactants}} = \frac{\sum_{i=1}^{N(\text{reactants})} n_i \left( [\tilde{h}(T) - \tilde{h}_{298}]_i + \Delta \tilde{h}_{f,i}^\circ \right)}{\sum_{i=1}^{N(\text{reactants})} n_i M_i} = h_{\text{products}} = \frac{\sum_{i=1}^{N(\text{products})} n_i \left( [\tilde{h}(T) - \tilde{h}_{298}]_i + \Delta \tilde{h}_{f,i}^\circ \right)}{\sum_{i=1}^{N(\text{products})} n_i M_i}$$

## Chemical equilibrium - hydrocarbons

- This set of 12 simultaneous nonlinear algebraic equations looks hopeless, but computer programs (using somewhat different methods more amenable to automation) (e.g. [GASEQ](http://gaseq.co.uk)) (gaseq.co.uk) exist
- Typical result, for stoichiometric CH<sub>4</sub>-air, 1 atm, constant P

Reactants			
Species	No. Moles	MolFrac	K
N <sub>2</sub>	0.79000	0.71493	
O <sub>2</sub>	0.21000	0.19005	
CH <sub>4</sub>	0.10500	0.09502	

Products			
Species	No. Moles	MolFrac	K
N <sub>2</sub>	0.78890	0.70864	
H <sub>2</sub> O	0.20413	0.18336	
CO <sub>2</sub>	0.09503	0.08536	
CO	0.00997	0.00896	
O <sub>2</sub>	0.00508	4.56e-03	
OH	0.00325	2.92e-03	
H	4.340e-04	3.90e-04	
O	2.371e-04	2.13e-04	
H <sub>2</sub>	0.00403	3.62e-03	
NO	0.00220	1.98e-03	

Reactants	Products
300.	Temperature, K 2226.
1.0	Pressure, atm 1.0
	Volume Products/Reactants 7.4754
	Moles Products/Reactants 1.00747
-1.688	H <sub>0</sub> , kcal/mol -1.675
47.857	S <sub>0</sub> , cal/mol/K 64.735
7.102	C <sub>p</sub> , cal/mol/K 9.896
1.389	Gamma, Cp/Cv 1.251
27.64	Mean Molecular Weight, g 27.43
1.1226	Density, kg/m <sup>3</sup> 0.15017
353.9	Sound speed, m/s 918.6
-61.07	Enthalpy, H, kcal/kg -61.07
1731.74	Entropy, S, cal/kg/K 2360.00
-82.64	Intern Energy, U, kcal/kg -222.34
-580.59	Free Energy, G, kcal/kg -5314.39
256.97	C <sub>p</sub> , cal/kg/K 360.78
24.6178	Volume, m <sup>3</sup> 182.663
2.45E+19	Molecules/cc 3.30E+18
4.06E-05	Moles/cc 5.47E-06
1.80E-05	Viscosity, kg/m/s 7.08E-05
1.60E-05	Kinematic Visc, m <sup>2</sup> /s 4.72E-04
5.79E-03	ThermCond, cal/m/K/s 3.16E-02
2.01E-05	ThDiffusivity, m <sup>2</sup> /s 5.84E-04

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15

## Chemical equilibrium - hydrocarbons

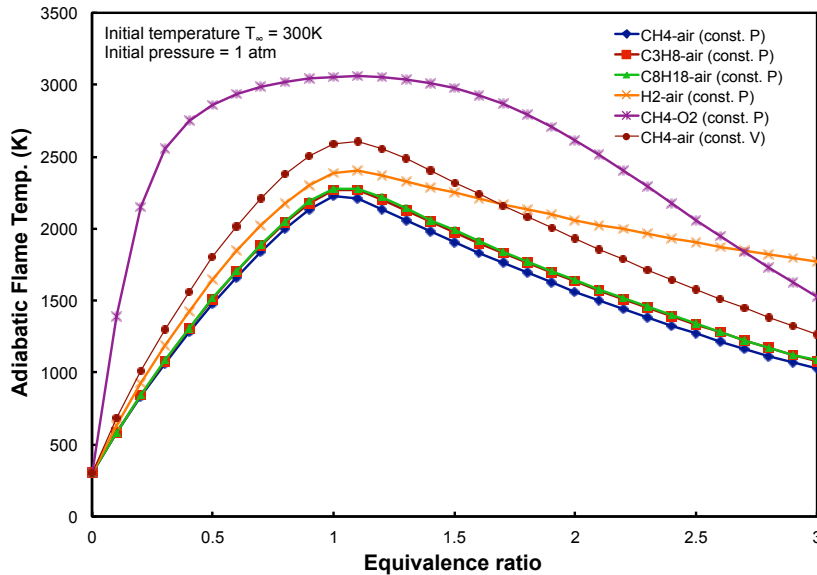
- Most of products are CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub> but some dissociation (into the other 7 species) occurs
- Product  $\gamma$  is much lower than reactants - affects estimation of compression / expansion processes using  $Pv^\gamma$  relations
- Implications for pollutant formation
  - Bad things like NO and CO appear in relatively high concentrations in products, but will recombine to some extent during expansion
  - By the time the expansion is completed, according to equilibrium calculations, practically all of the NO and CO should disappear, but in reality they don't - as T and P decrease during expansion, reaction rates decrease, thus at some point the reaction becomes "frozen", leaving NO and CO "stuck" at concentrations MUCH higher than equilibrium
  - Discussed in detail in Lecture 5

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16



## Adiabatic flame temp. - hydrocarbons



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17

## Adiabatic flame temp - hydrocarbons

- Adiabatic flame temperature ( $T_{ad}$ ) peaks slightly rich of stoichiometric - since  $O_2$  is highly diluted with  $N_2$ , burning slightly rich ensures all of  $O_2$  is consumed without adding much extra unburnable molecules
- $T_{ad}$  peaks at  $\approx 2200\text{K}$  for  $CH_4$ , slightly higher for  $C_3H_8$ , iso-octane ( $C_8H_{18}$ ) virtually same as  $C_3H_8$
- $H_2$  has far heating value per unit fuel mass, but only slightly higher per unit total mass (due to “heavy” air), so  $T_{ad}$  not much higher
  - Also - massive dissociation as  $T$  increases above  $\approx 2400\text{K}$ , keeps peak temperature down near stoichiometric
  - Also - since stoichiometric is already 29.6%  $H_2$  in air (vs. 9.52% for  $CH_4$ , 4.03% for  $C_3H_8$ ), going richer does not add many extra fuel molecules
- $CH_4 - O_2$  MUCH higher - no  $N_2$  to soak up thermal energy without contributing enthalpy release
- Constant volume - same trends but higher  $T_{ad}$

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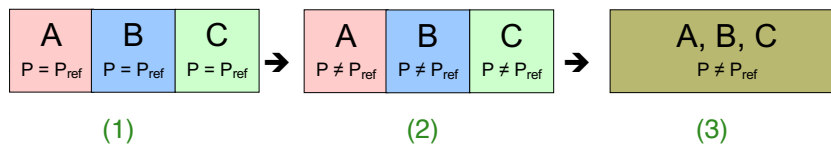
18

## Compression / expansion

- Compression / expansion assumed to occur at constant entropy (not constant h or u)
- Three levels of approximation
  - Frozen composition (no change in  $X_i$ 's): **infinitely slow reaction**
  - Equilibrium composition ( $X_i$ 's change to new equilibrium) corresponds to **infinitely fast reaction** (since once we get to equilibrium, no further change in composition can occur)
  - Reacting composition (finite reaction rate, not infinitely fast or slow) - more like reality but MUCH more difficult to analyze since **rate equations** for 100s or 1000s of reactions are involved
- Which gives best performance?
  - Equilibrium – you're getting everything the gas has to offer; **recombination** (e.g.  $H + OH \rightarrow H_2O$ ) gives extra thermal enthalpy release, more push on piston or more exhaust kinetic energy
  - Frozen - no recombination, no extra enthalpy release
  - Reacting - somewhere between, most realistic

## Entropy of an ideal gas mixture

- S depends on P AND T (unlike H and U, which depend ONLY on T)



- (1) Start with gases A, B and C at temperature T and  $P_o = 1$  atm
 
$$S = S_A + S_B + S_C = n_A \Delta \tilde{s}_A^o(T) + n_B \Delta \tilde{s}_B^o(T) + n_C \Delta \tilde{s}_C^o(T) = \sum_{i=1}^N n_i \Delta \tilde{s}_i^o(T)$$

$S$  = total entropy of all gases;  $n_i$  = moles of species  $i$ ;  $N$  = number of species  
 $\Delta \tilde{s}_i^o(T)$  = entropy **per mole** of  $i$  at any temperature T & ref. pressure = 1 atm
- Recall (Lecture 1, review of thermodynamics) that for an ideal gas

$$\tilde{S}_2 - \tilde{S}_1 = \tilde{C}_p \ln\left(\frac{T_2}{T_1}\right) - \mathfrak{R} \ln\left(\frac{P_2}{P_1}\right)$$

## Entropy of an ideal gas mixture

- (2) Raise/lower each gas to pressure  $P \neq 1$  atm (same  $P$  for all)

$$\Delta S_A = n_A [\tilde{C}_p \ln(T_2/T_1) - \Re \ln(P_2/P_1)] = n_A [\tilde{C}_p \ln(T/T) - \Re \ln(P/P_{ref})] = -n_A \Re \ln(P/P_{ref})$$

$$S = \sum_{i=1}^N n_i \Delta \tilde{s}_i^o(T) - \sum_{i=1}^N n_i \Re \ln(P/P_{ref}) = \sum_{i=1}^N n_i [\Delta \tilde{s}_i^o(T) - \Re \ln(P/P_{ref})] = \sum_{i=1}^N n_i \Delta \tilde{s}_i^o(T) - n_T \Re \ln(P/P_{ref})$$

- (3) Now remove dividers,  $V_A \rightarrow V_A + V_B + V_C$  ( $V$  = volume)

$$S = \sum_{i=1}^N n_i [\Delta \tilde{s}_i^o(T) - \Re \ln X_i] - n_T \Re \ln(P/P_{ref}) = \sum_{i=1}^N n_i [\Delta \tilde{s}_i^o(T) - \Re \ln X_i - \Re \ln(P/P_{ref})]$$

$$= \sum_{i=1}^N n_i [\Delta \tilde{s}_i^o(T) - \Re \ln(P_i/P_{ref})]$$

- Can also combine  $X_i$  and  $P/P_{ref}$  terms using **partial pressures**  $P_i$ ; for an ideal gas mixture  $X_i = P_i/P$ , where (as above)  $P$  without subscripts is the total pressure =  $\sum P_i$

$$\Delta S_A = n_A [\tilde{C}_p \ln(T_2/T_1) + \Re \ln(V_2/V_1)] = n_A [\tilde{C}_p \ln(T/T) + \Re \ln((V_A + V_B + V_C)/V_A)]$$

$$= n_A \Re \ln((n_A + n_B + n_C)/n_A) = -n_A \Re \ln(n_A/n_T); \text{ recall } X_A \equiv n_A/n_T = \text{mole fraction of A}$$

$$S = \sum_{i=1}^N n_i \Delta \tilde{s}_i^o(T) - n_T \Re \ln(P/P_{ref}) - \sum_{i=1}^N \Re n_i \ln(n_i/n_T) = \sum_{i=1}^N n_i [\Delta \tilde{s}_i^o(T) - \Re \ln X_i] - n_T \Re \ln(P/P_{ref})$$

AME 436 - Spring 2019 - Lecture 3 - Chemical Thermodynamics 2

21

## Compression / expansion

- Most useful form in terms of  $s = S/m$ , since mass ( $m$ ) is constant

$$s = \frac{\sum_{i=1}^N X_i (\Delta \tilde{s}_i^o(T) - \Re \ln X_i) - \Re \ln(P/P_{ref})}{\sum_{i=1}^N X_i M_i} \quad \left( \text{units } \frac{J}{kg \cdot K} \right)$$

$\Delta \tilde{s}_i^o(T)$  = entropy of species  $i$  at reference pressure (1 atm) and temperature  $T$  (not necessarily 298K) (see the Excel tables)

$\Re \ln(P/P_{ref})$  - entropy associated with pressure different from 1 atm;  
 $P > P_{ref}$  leads to decrease in  $s$  (again,  $P_{ref} = 1$  atm)

$\Re X_i \ln(X_i)$  - entropy associated with mixing ( $X_i < 1$  means more than 1 specie is present - always leads to increase in entropy since  $-X_i \ln(X_i) > 0$ )

- Denominator is just the average molecular mass

- Use  $s_{\text{reactants}} = s_{\text{products}}$  for compression / expansion
- All other relations (atom ratio constraints,  $\sum X_i = 1$ , equilibrium constraints) still apply for compression & expansion processes

AME 436 - Spring 2019 - Lecture 3 - Chemical Thermodynamics 2

22

## Compression / expansion

- Example - expansion of CO<sub>2</sub>-O<sub>2</sub>-CO mixture from 10 atm, 2500K to 1 atm in steady-flow control volume (e.g. nozzle) or control mass (e.g piston/cylinder)
- Initial state (mixture from lecture 2 where h was calculated):

$$X_{CO} = 0.0129, X_{O_2} = 0.3376, X_{CO_2} = 0.6495, T = 2500, P = 10 \text{ atm}$$

$$h = -3784 \text{ kJ/kg}, u = -4397 \text{ kJ/kg}$$

$$\Delta \tilde{s}_{CO}^{\circ}(T) = 266.755 \text{ J / moleK}; \Delta \tilde{s}_{O_2}^{\circ}(T) = 277.207 \text{ J / moleK};$$

$$\Delta \tilde{s}_{CO_2}^{\circ}(T) = 322.808 \text{ J / moleK}; \mathfrak{R} = 8.314 \text{ J / moleK}$$

$$s = \frac{X_{CO}(\Delta \tilde{s}_{CO}^{\circ} - \mathfrak{R} \ln X_{CO}) + X_{O_2}(\Delta \tilde{s}_{O_2}^{\circ} - \mathfrak{R} \ln X_{O_2}) + X_{CO_2}(\Delta \tilde{s}_{CO_2}^{\circ} - \mathfrak{R} \ln X_{CO_2}) - \mathfrak{R} \ln(P / P_{ref})}{X_{CO}M_{CO} + X_{O_2}M_{O_2} + X_{CO_2}M_{CO_2}}$$

$$s = \frac{(0.0129)(266.755 - 8.314 \ln(0.0602)) + (0.3376)(277.207 - 8.314 \ln(0.3376)) + (0.6495)(322.808 - 8.314 \ln(0.6495)) - 8.314 \ln(10/1)}{(0.0129)(0.028) + (0.3376)(0.032) + (0.6495)(0.044)}$$

$$s = 7382 \text{ J / kgK}$$

## Compression / expansion

- Expand at **constant entropy** to 1 atm, **frozen composition**:

$$T = 1738\text{K}, X_{CO} = 0.0129, X_{O_2} = 0.3376, X_{CO_2} = 0.6495,$$

$$h = -4795 \text{ kJ/kg}, u = -5159 \text{ kJ/kg}, s = 7381 \text{ J/kgK}$$

- Work done (control volume, steady flow)  
=  $h_{\text{before}} - h_{\text{after}} = +1011 \text{ kJ/kg}$
- Work done (control mass) =  $u_{\text{before}} - u_{\text{after}} = +762 \text{ kJ/kg}$

- Expand at **constant entropy** to 1 atm, **equilibrium composition**:

$$T = 1794\text{K}, X_{CO} = 0.00022, X_{O_2} = 0.3334, X_{CO_2} = 0.6664$$

(significant recombination)

$$h = -4811 \text{ kJ/kg}, u = -5184 \text{ kJ/kg}, s = 7382 \text{ J/kgK}$$

- Work done (control volume, steady flow) =  $+1027 \text{ kJ/kg}$   
(1.6% higher)
- Work done (control mass) =  $787 \text{ kJ/kg}$  (3.3% higher)

- Moral: let your molecules recombine!

### Summary - Lecture 3

- In order to understand what happens to a chemically reacting mixture **if we wait a very long time**, we need to apply
  - 1st Law of Thermodynamics (conservation of energy) - but this doesn't tell us what the allowable direction of the reaction is;  $A \rightarrow B$  or  $B \rightarrow A$  are equally valid according to the 1st Law
  - 2nd Law of Thermodynamics (increasing entropy) - invokes restrictions on the direction of allowable processes (if  $A \rightarrow B$  is allowed then  $B \rightarrow A$  isn't, unless it's an isentropic process)
- **Equilibrium** occurs when the worst possible end state is reached; once this point is reached, no further chemical reaction is possible unless something is changed, e.g. T, P, V, etc.
- The consequences of the 2nd law are
  - $ds \geq 0$  (constant u & v, e.g. a rigid, insulated box)
  - $dg = d(h - Ts) \leq 0$  (constant T and P, e.g. isothermal piston/cylinder)
  - $ds = 0$  (reversible adiabatic compression / expansion)

### Summary - Lecture 3

- The application of the 2nd law leads to complicated-looking expressions called **equilibrium constraints** that involve the concentrations of each type of molecule present in the mixture
- For a system with N types of molecules and M types of atoms, the number of unknowns is the mole fractions of each species  $X_i$ , temperature T and Pressure P (total **N + 2** unknowns)
- The equations required to satisfy chemical equilibrium and determine the end state of the system, *i.e.*, the combustion products is
  - **N - M** equilibrium constraint equations
  - **M - 1** atom ratio constraints
  - **1** sum of all mole fractions =  $\sum X_i = 1$
  - **1** Ideal gas law (or other equations of state, not discussed in this class) (not needed if pressure is specified)
  - **1** conservation of energy (not needed if temperature is specified)
  - Total **N + 2** equations

## Summary - Lecture 3

- Compression – assumed “frozen” otherwise game over before it starts!
- Combustion - adiabatic flame temperature ( $T_{ad}$ ) peaks near stoichiometric; higher for
  - Constant V vs. constant P (no PdV work in constant V case)
  - $O_2$  vs. air (no  $N_2$  dilution)
  - $H_2$  vs. hydrocarbons (higher  $Q_R$ )
- Expansion – can assume
  - Frozen – no reaction, no recombination, no extra enthalpy release
  - Equilibrium – infinitely fast reaction, maximum recombination & extra enthalpy release
  - Reacting at finite rates - somewhere between, most realistic, hardest to compute