

Lecture # 7

Chemical Thermodynamics 3

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February 24, 2020

- Adiabatic Combustion
- Gasification
- Availability Loss in adiabatic combustion
- Combustion Engine Efficiency
- Maximum possible efficiency using chemical energy

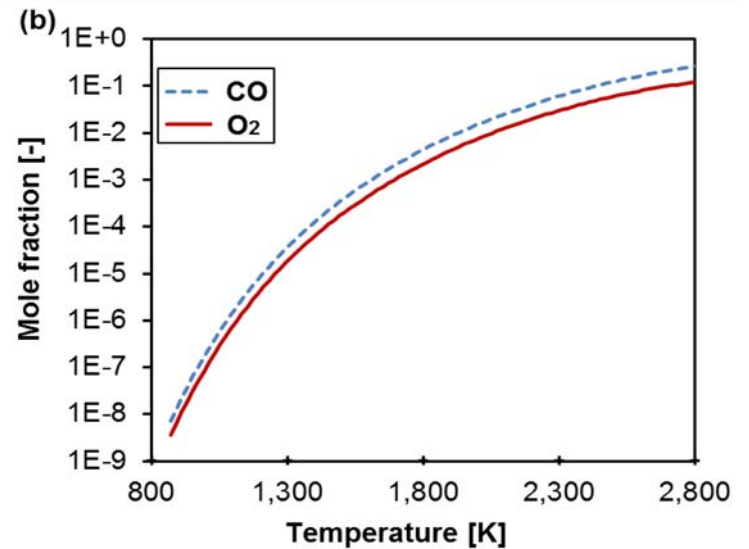
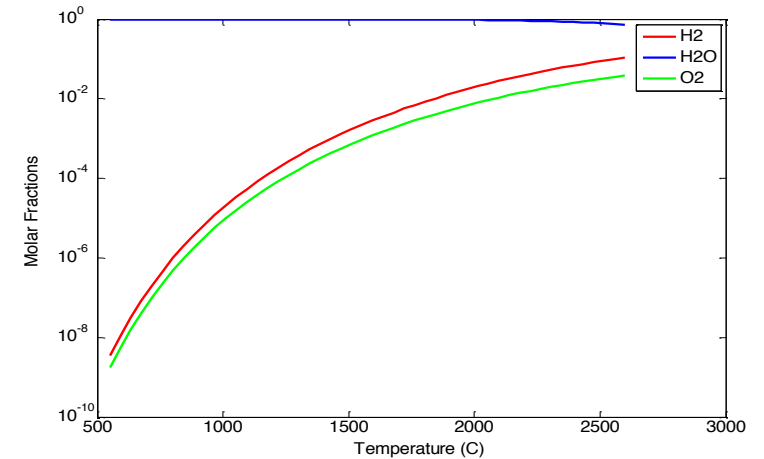
Mixtrure has: $\chi_1, \chi_2, \chi_3, \dots, \chi_n$

Some components can participate in one or more reactions:

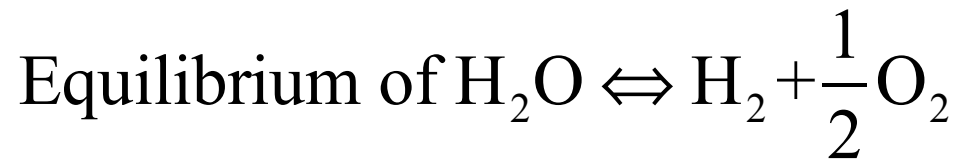
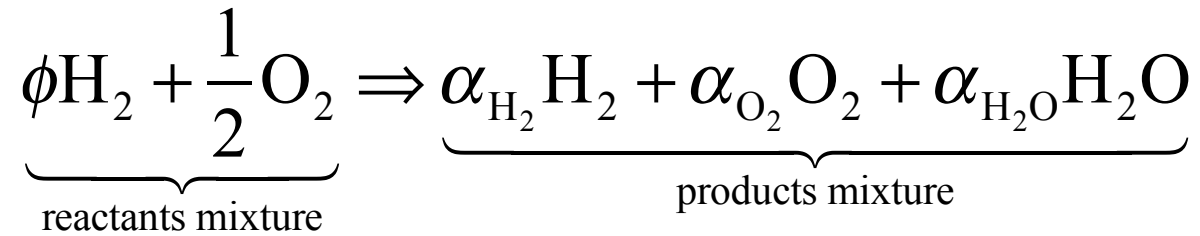
$$\underbrace{\sum_{j=1}^J v_j' \chi_j}_{\text{reactants}} \Rightarrow \underbrace{\sum_{j=1}^J v_j'' \chi_j}_{\text{products}}, \text{ then } \frac{\left(\prod_{j=1}^J p_j^{v_j''} \right)_{\text{products}}}{\left(\prod_{j=1}^J p_j^{v_j'} \right)_{\text{reactants}}} = K_p(T),$$

$$\frac{\prod_{\text{prod}} X_j^{v_j''}}{\prod_{\text{react}} X_j^{v_j'}} = \frac{K_p(T)}{p^\sigma} \quad \text{where} \quad \sigma = \sum_{\text{prod}} v_j'' - \sum_{\text{react}} v_j'$$

Equilibrium driven dissociation of H₂O (top) and of CO₂ (bottom) at high T

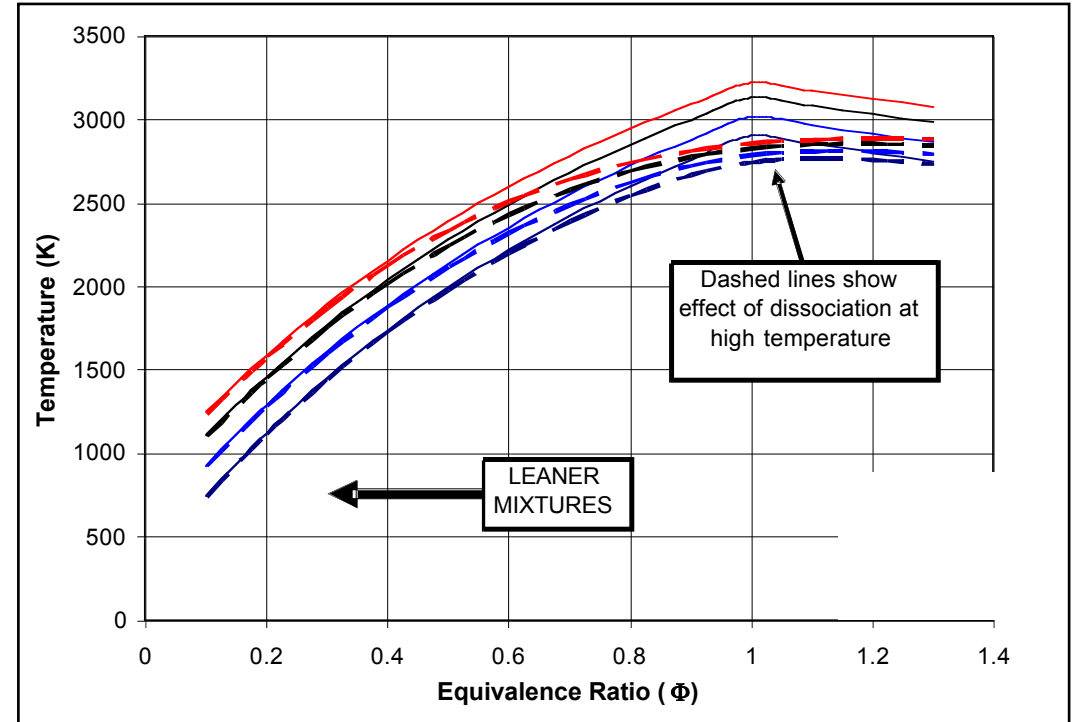


Adiabatic Combustion of Hydrogen-Oxygen, and their Flame temperature

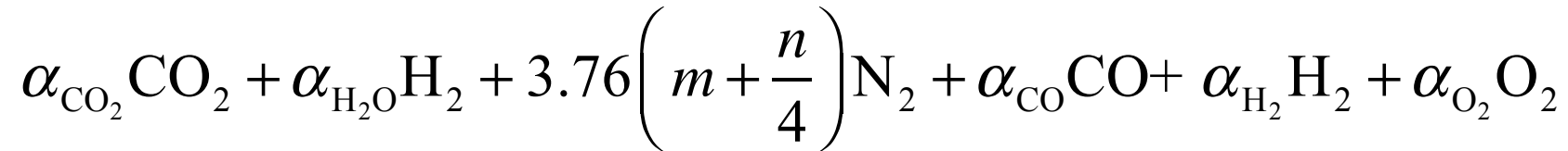
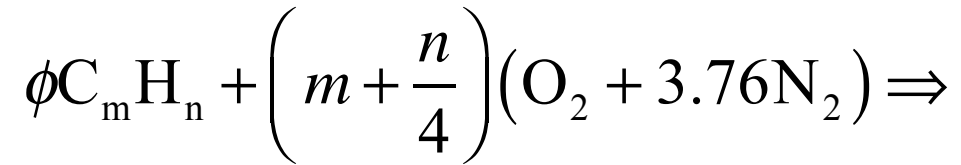


and + the energy equation ...

$$\sum_{\text{react mix}} n_i \hat{h}_i(T_r) = \sum_{\text{prod mix}} n_i \hat{h}_i(T_p)$$



Computing products of combustion of HC combustion using equilibrium constants



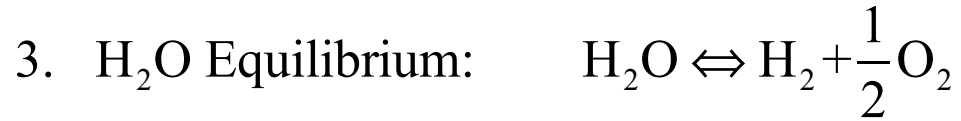
six unknowns (including T):

1. Mass conservation (3 equations) $m = \alpha_{CO_2} + \alpha_{CO}$, and $n = 2(\alpha_{H_2O} + \alpha_{H_2})$

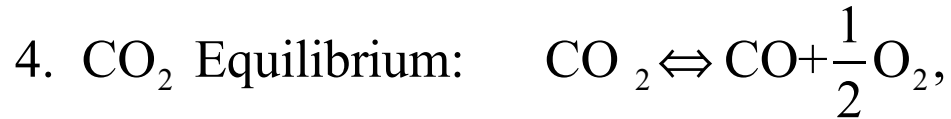
and $\left(m + \frac{n}{4}\right) = \alpha_{CO_2} + \frac{1}{2}\alpha_{CO} + \frac{1}{2}\alpha_{H_2O} + \alpha_{O_2}$ (note that: $X_i = \alpha_i / \sum \alpha_i$)

2. Energy Conservation (constant H): $\sum_{react} \nu_i \hat{h}_i(T_1) = \sum_{prod} \alpha_i \hat{h}_i(T_p)$

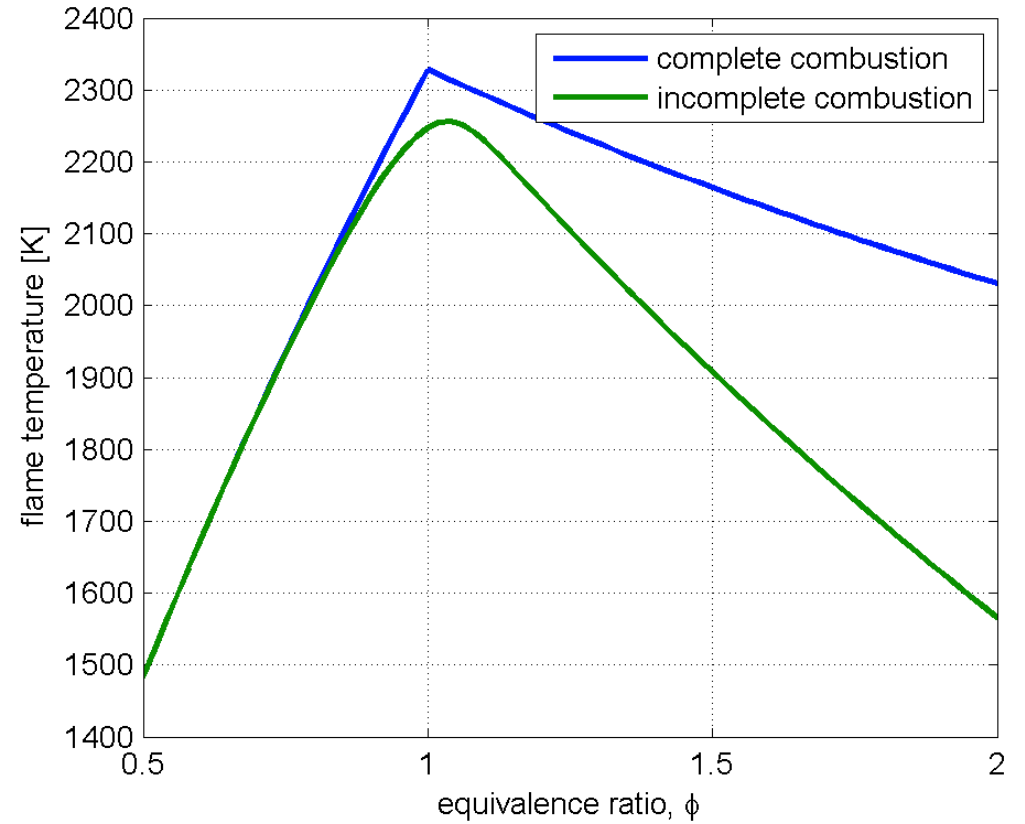
Important Reactions



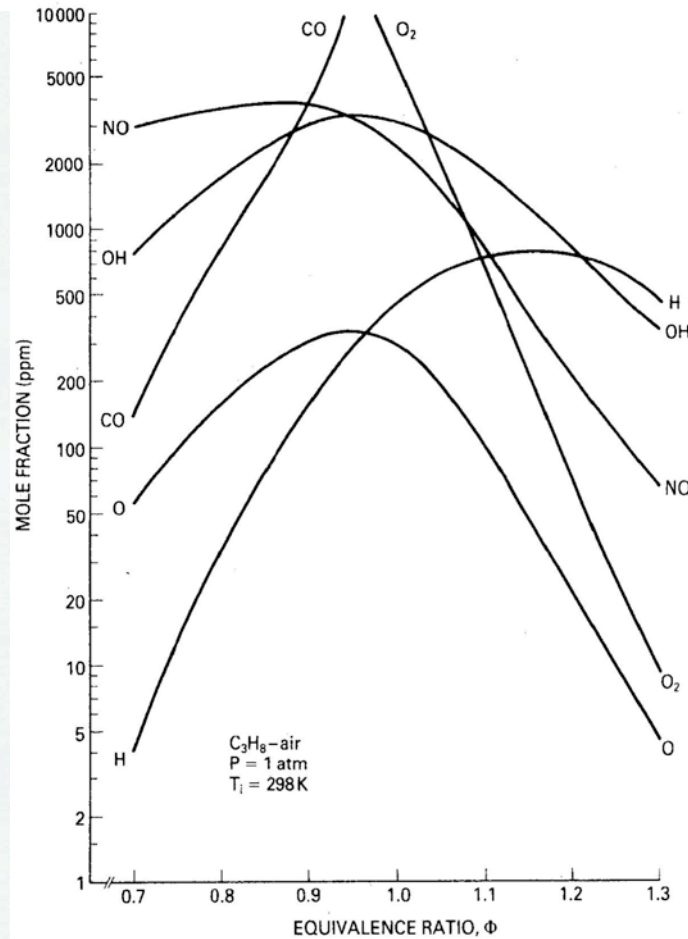
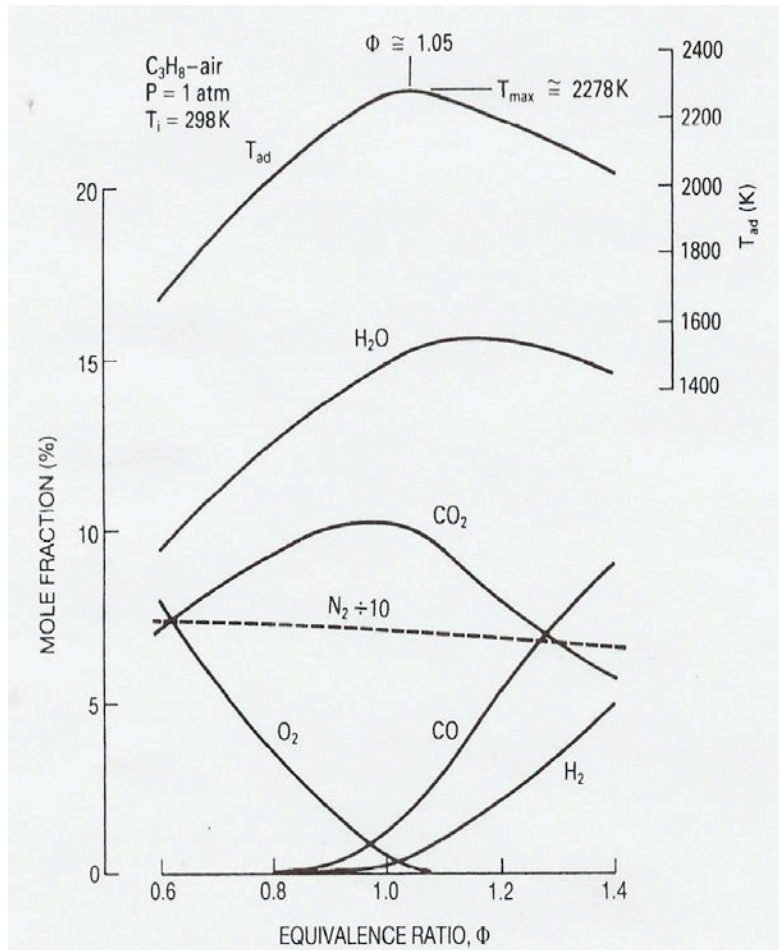
$$\frac{X_{\text{H}_2} X_{\text{O}_2}^{1/2}}{X_{\text{H}_2\text{O}}} = \frac{K_p}{\sqrt{p}}, \quad K_p(T) = \exp\left(-\frac{\Delta G_{R, \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2}^o(T)}{\mathfrak{R}T}\right)$$



$$\frac{X_{\text{CO}} X_{\text{O}_2}^{1/2}}{X_{\text{CO}_2}} = \frac{K_p}{p^{1/2}}, \quad K_p(T) = \exp\left(-\frac{\Delta G_{R, \text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2}^o(T)}{\mathfrak{R}T}\right)$$



Methane combustion in air



If oxygen is not present in products,
or is negligible ($\phi \geq 1$)
then one reaction is sufficient:

Homogeneous water-gas equilibrium:



$$\text{and } \frac{X_{\text{H}_2} X_{\text{CO}_2}}{X_{\text{H}_2\text{O}} X_{\text{CO}}} = K_p,$$

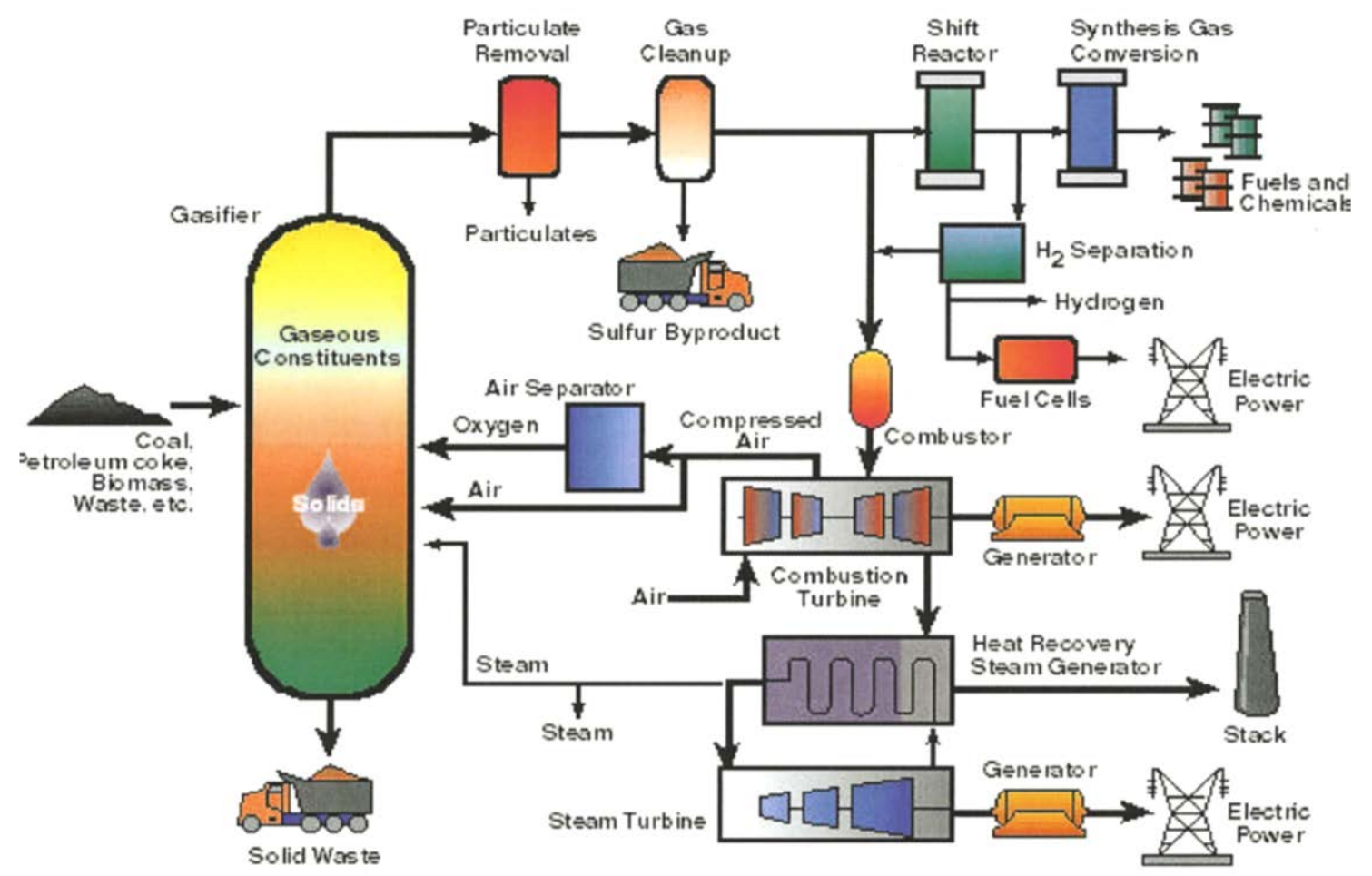
with $K_{p, \text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{H}_2 + \text{CO}}(T) =$

$$\exp\left(-\frac{\Delta G_{R, \text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{H}_2 + \text{CO}}^{\circ}(T)}{\mathcal{R}T}\right)$$

For NO, $\frac{1}{2}\text{O}_2 + \frac{1}{2}\text{N}_2 \rightleftharpoons \text{NO},$

But NO hardly reaches equilibrium

Coal Gasification and IGCC (also “Clean Coal!”) and pre-combustion CO₂ Capture



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Coal Gasification Reactions

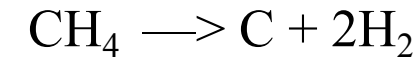
Heating value of coal, 14-35 MJ/kg, or 168-420 MJ/kmol depends on its type

		MJ/kgmol	
Partial oxidation $C + \frac{1}{2} O_2 \rightarrow CO$	← with p ↑	-123.1	Provides gasification heat
combustion $C + O_2 \rightarrow CO_2$		-393.6	Provides more gasification heat
Boudouard reaction $C + CO_2 \rightarrow 2CO$	← with p ↑ → with T ↑	159.91	Gasification reaction
Heterogeneous shift reaction $C + H_2O \rightarrow CO + H_2$	← with p ↑ → with T ↑	118.5	Gasification reaction
methane formation $C + 2H_2 \rightarrow CH_4$	→ with p ↑ ← with T ↑	-87.5	
Homogeneous shift reaction $CO + H_2O \rightarrow CO_2 + H_2$	← with T ↑	-40.9	
Methanation reaction $CO + 3H_2 \rightarrow CH_4 + H_2O$	→ with p ↑ ← with T ↑	-205.9	

Gottlicher, The Energetics of Carbon Dioxide Capture in Power Plants, DOE, 2004

Courtesy of DOE.

Methane Pyrolysis (for C and H₂ production)



- One kmol of CH₄ (LHV=800 MJ/kmol) results in 2 kmol H₂ (total LHV=2x240=480 MJ) and 1 kmol of C (HV=394 MJ) and requires ~ 80 MJ/kmol (difference between the products and reactants total enthalpy).
- Total H₂ energy (480 MJ) is 60% of what we had originally.

Because of heat transfer processes and gas separation in synthetic fuel production, system integration is important for raising the overall reforming efficiency ...

$$\eta_{reform} = \frac{\text{chemical energy out (+ thermal !)}}{\text{chemical (and thermal) energy in+separation work}}$$

$$= \frac{(\dot{n}_f \Delta \hat{h}_f)_{out} + \dot{Q}_{out}}{\sum_{in} (\dot{n}_f \Delta \hat{h}_f) + \dot{Q}_{in} + \dot{E}_{sep}}$$

\dot{E}_{sep} should be measured in terms of "heat equivalent"

- High efficiency heat exchangers are needed.
- Cost is high, integration justifiable for large production.
- Less so for local operation or mobile applications.
- Progress and innovation are underway.

Efficiency of Synthetic Fuel Production

Fuel	Product	Efficiency
Coal	syngas	72-87%
Coal	methane	61-78
Coal	Methanol	51-59
Coal	Hydrogen	62
Oil	Hydrogen	77
Methane	Hydrogen	70-79
Coal/Oil/Gas	Hydrogen (E)	20-30
Oil Shale	Oil/Gas	66-72
Methanol	Oil/gas	86
Wood	Gas	90
Corn	Ethanol	46
Manure	Gas	90

Fay and Colomb, Energy and the Environment, 2000.

Courtesy of EPA.

1. Chemical energy can be converted to thermal energy or heat at nearly 100% efficiency (some equilibrium limitations).
2. Chemical Energy can be converted to other forms of chemical energy, typically conversion is limited by equilibrium which is T (and p) dependent, but at < 100 % due to losses in the system. If other chemicals are produced, separation energy further reduces the output.
3. Chemical energy can be converted to work in
 1. Combustion engine, entropy loss in combustion lowers efficiency.
 2. Directly, through electrochemical reaction, nearly isothermally, lowering entropy generation. What is this?

IMPACT OF ENTROPY GENERATION IN REACTIONS

Adiabatic Combustion involves entropy generation and loss of availability, but raises the temperature to values suitable for the operation of heat engines.

adiabatic flame temperature, pressure, entropy generation, and composition of some of the product gases for combustion of isooctane, C_8H_{18} , in a **perfectly insulated constant-volume combustion chamber**, Gyftopoulos and Beretta

For adiabatic reactions:

$$\Delta S_R = \Delta S_g = \sum_{\text{prod mix}} n_i \hat{s}_i(T, p, X_i) - \sum_{\text{react mix}} n_i \hat{s}_i(T, p, X_i)$$

OR
$$\Delta S_g = S_p(T_F, p_p) - S_r(T^*, p^*)$$

λ	T_b K	p_b atm	$\frac{T_o S_{irr}}{(-n_{1a} \Delta g^o)}$ %	CO_2 kmol MJ	CO mol MJ	H_2 mol MJ
1.0	2912	44.8	20.8	1.17	357	73.8
1.1	2843	43.2	21.5	1.30	230	44.9
1.2	2758	41.5	22.1	1.39	143	27.6
1.3	2667	39.9	22.8	1.44	86.8	17.0
1.4	2577	38.4	23.4	1.48	52.1	10.5
1.5	2489	37.0	23.9	1.50	31.4	6.60
1.6	2408	35.7	24.5	1.51	19.0	4.19
1.7	2332	34.5	25.0	1.52	11.7	2.70
1.8	2262	33.4	25.4	1.52	7.28	1.78
1.9	2198	32.4	25.9	1.53	4.61	1.19
2.0	2138	31.4	26.3	1.53	2.96	0.78

mixture of isooctane and dry air is at $T_a = 700$ K and $p_a = 10$ atm.

Work interaction in a Process undergoing Chemical Reaction

steady state, flow process

$$Q - W = H_{out} - H_{in}$$

$$0 = \frac{Q}{T^*} + S_{in} - S_{out} + \Delta S_g$$

$$W_{chem.eng.} = (H_1 - T^* S_1) - (H_2 - T^* S_2) - T^* \Delta S_g$$

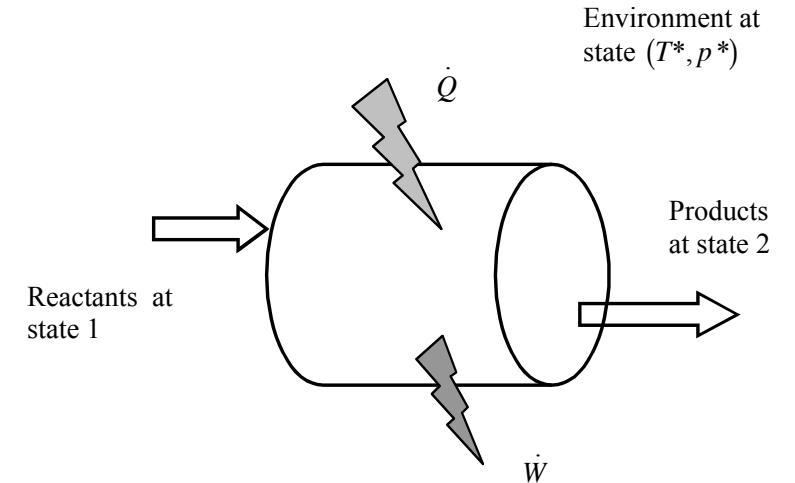
(availability-Irreversibility)

reactants at state 1 and products at state 2:

$$W = \sum_{react} n_i \left(\hat{h}_i(T_1) - T^* \hat{s}_i(T_1, p_{i,1}) \right) - \sum_{prod} n_i \left(\hat{h}_i(T_2) - T^* \hat{s}_i(T_2, p_{i,2}) \right) - T^* \Delta S_g$$

Maximum Work, $\Delta S_g \rightarrow 0$

$$W_{max.chem.eng} = \sum_{react,1} v_i' (\hat{h}_i - T^* \hat{s}_i) - \sum_{prod,2} v_i'' (\hat{h}_i^* - T^* \hat{s}_i^*)$$



"Largest" Maximum work:

exit stream at mechanical, thermal
and chemical equilibrium with environment,

If inlet and exit streams are both at

mechanical and thermal equilibrium

with the environment $(T_o, p_o) = (T^o, p^o)$:

$$\begin{aligned} W_{\max} &= \sum_{\text{react}} v_i' \left(\hat{h}_i(T_o) - T_o \hat{s}_i(T_o, p_{o,i}) \right) \\ &\quad - \sum_{\text{prod}} v_i'' \left(\hat{h}_i(T_o) - T_o \hat{s}_i(T_o, p_{o,i}) \right) \\ &= -\Delta G_R^o(T_o, p_{o,i}) = -\Delta G_R^{\text{avail}}(T_o, p_{o,i}) \end{aligned}$$

Since $p_o = 1 \text{ atm}$,

$$\begin{aligned} (-\Delta G_R^{\text{avail}}) &= (-\Delta G_R^{oo}(T_o)) + \Re T_o \ln \left(\prod_{\text{react}} X_i^{v_i'} / \prod_{\text{prod}} X_i^{v_i''} \right) \\ &\approx \Delta G_R^{oo} \end{aligned}$$

Calculations show that $\Delta G_R^{oo} \approx \Delta H_{R,LHV}^o$

Fuel (phase) ^b	$-\Delta H_R^o$ (for LHV) kJ/mol	$-\Delta H_R^o$ (for HHV) kJ/mol	$-\Delta G_R^{oo}(T^o, p^o)$ (kJ/mol)	$\hat{\xi}_{\text{fuel}}^o$ (kJ/mol)
Hydrogen (g), H ₂	241.8	285.9	228.6	235.2
Carbon (s), C	393.5	393.5	394.4	410.5
<i>Paraffin (alkane) Family, C_n H_{2n+2}</i>				
Methane (g), CH ₄	802.3	890.4	818	830.2
Ethane (g), C ₂ H ₆	1427.9	1559.9	1467.5	1493.9
Propane (g), C ₃ H ₈	2044	2220	2108.4	2149
Butane (g), C ₄ H ₁₀	2658.5	2878.5	2747.8	2802.5
Pentane (g), C ₅ H ₁₂	3272.1	3536.1	3386.9	3455.8
Pentane (l), C ₅ H ₁₂	3245.5	3509.5	3385.8	3454.8
Hexane (g), C ₆ H ₁₄	3886.7	4194.8	4026.8	4110
Hexane (l), C ₆ H ₁₄	3855.1	4163.1	4022.8	4106
Heptane (g), C ₇ H ₁₆	4501.4	4853.5	4667	4764.3
Heptane (l), C ₇ H ₁₆	4464.9	4816.9	4660	4757.3
Octane (g), C ₈ H ₁₈	5116.2	5512.2	5307.1	5418.6
Octane (l), C ₈ H ₁₈	5074.6	5470.7	5297.2	5408.7

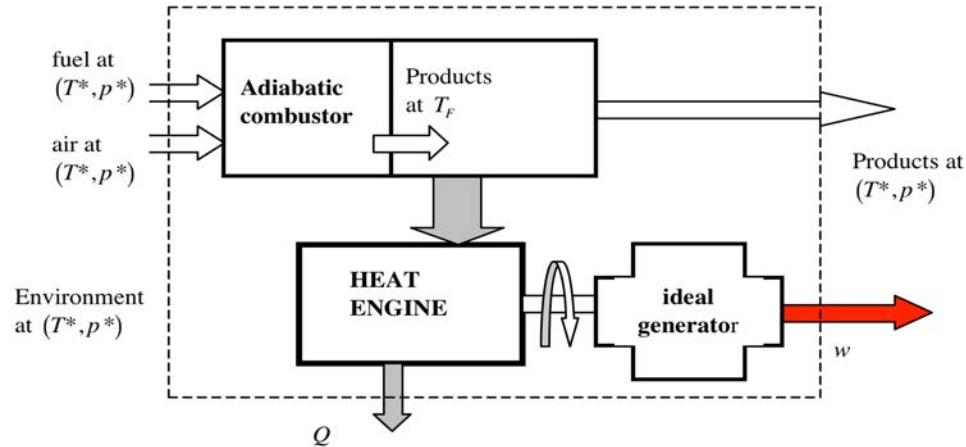
$$\hat{\xi}_{\text{fuel}}^o = (-\Delta G_R^{oo}) + \Re T_o \ln \left(\prod_{\text{react} \neq \text{fuel}} (X_i^o)^{v_i'} / \prod_{\text{prod}} (X_i^o)^{v_i''} \right) \approx (-\Delta G_{R,\text{fuel}}^{oo})$$

X_i^o are evaluated for standard concentrations (except for the fuel)

Bejan, Advanced Eng. Thermo., Wiley 1988 and Moran, Availability Analysis, Prentice Hall 1982

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Combustion Engine Work and Efficiency



Another model uses:

$$\eta_{car} = 1 - \ln \frac{T_F}{T^*} / \left(\frac{T_F}{T^*} - 1 \right)$$

$$= 70\% \text{ for } T_F / T^* = 8$$

$$W_{\max} = \eta_{car} |\Delta H_R|$$

A Possible Model:

$$\begin{aligned} W_{\max, \text{comb. eng.}} &= W_{\max, \text{chem. eng.}} - T^* \Delta S_{\text{ad. comb.}} \\ &= (H_1 - T^* S_1) - (H_2 - T^* S_2) - T^* \Delta S_g \\ &= (H_1 - T^* S_1) - (H_2 - T^* S_2) - T^* (S_F - S_1) \\ &= (H_F - T^* S_F) - (H_2 - T^* S_2) (= W_{car}(T_F, T^*)) \end{aligned}$$

$$(\eta_{\text{best. comb.}})_{\text{sec Law}} = \frac{W_{\max, \text{comb. eng.}}}{\Delta G_R^o} = \frac{W_{\max, \text{chem. eng.}}^*}{\Delta G_R^o} - \left| \frac{T_o \Delta S_{\text{ad. comb.}}}{\Delta G_R^o} \right|$$

$$(\eta_{\text{best. comb.}})_{\text{sec Law}} \approx \frac{W_{\max, \text{chem. eng.}}^*}{\Delta G_R^o} - \underbrace{\left| \frac{T_o \Delta S_{\text{ad. comb.}}}{\Delta G_R^o} \right|}_{\text{See Tables}}$$

- The choice of T_F is tricky, its max is the adiabatic stoichiometric flame T , but the actual value depends on the equipment
- Another model uses the log mean temperature Carnot efficiency (T_F and T^*) and enthalpy of reaction for max W .
- Again the choice of T_F is tricky!

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