Lecture # 6
Chemical Thermodynamics 2
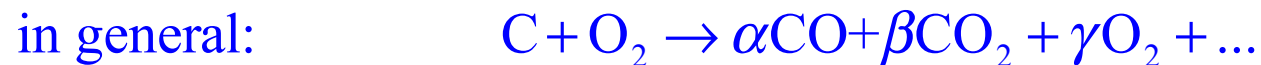# Ahmed F Ghoniem

February 19, 2020

Mass conservation determines the products composition if the number of components equals the number of distinct element.
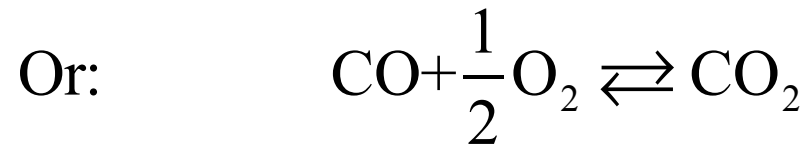Energy conservation determines the temperature, or the heat and work interactions.

What defines the product composition if the number of components is larger than the number of elements (rich burning, reforming, dissociation)?
Or how to determine the extent of the reaction (at equilibrium) as function of the conditions (T,p) and elemental composition?

complete oxidation: $C + O_2 \rightarrow CO_2$,   partial oxidation: $C + O_2 \rightarrow CO + \frac{1}{2}O_2$

in general: $C + O_2 \rightarrow \alpha CO + \beta CO_2 + \gamma O_2 + ...$

Chemical reactions can move both ways, forward and backward:

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \quad \text{and} \quad CO_2 \rightarrow CO + \frac{1}{2}O_2$$

Or: $\qquad CO + \frac{1}{2}O_2 \rightleftarrows CO_2$

that is the mixture of three components (CO, O_2, CO_2) can co-exist

the fractions depend on the thermodynamic state, e.g., (p, T)

The composition, or final state depends on the conditions, that is, pressure, temperature and amount originally existing in the mixture (elemental composition).

We need to find the rules of "Equilibrium".

How about Entropy ....

$$\frac{dS}{dt} = \sum_k \frac{\dot{Q}_k}{T_k} + \sum_{react} \dot{n}_i \hat{s}_i - \sum_{prod} \dot{n}_i \hat{s}_i + \dot{S}_g$$

$$\hat{s}_i(T, p, X_i) = \left(\hat{s}_i^{oo} + \int_{T^o}^T \frac{\hat{c}_{p,i}(T)}{T} dT \right) - \left(\Re \ell n \frac{p}{p^o} + \Re \ell n X_i \right)$$

For steady adiabatic reactions: $\Delta S_R = \Delta S_g = \sum_{prod} v_i'' s_i(T, p, X_i) - \sum_{react} v_i' s_i(T, p, X_i)$

For "spontaneous" reactions at constant $(H$ and $p)$, ΔS_g must be positive ..

General Condition for Equilibrium
Expressed in terms of Entropy Generation
the combined statment of the 1st and 2nd law

$$T\,dS_g = T\,dS - dU - p\,d\forall \geq 0$$
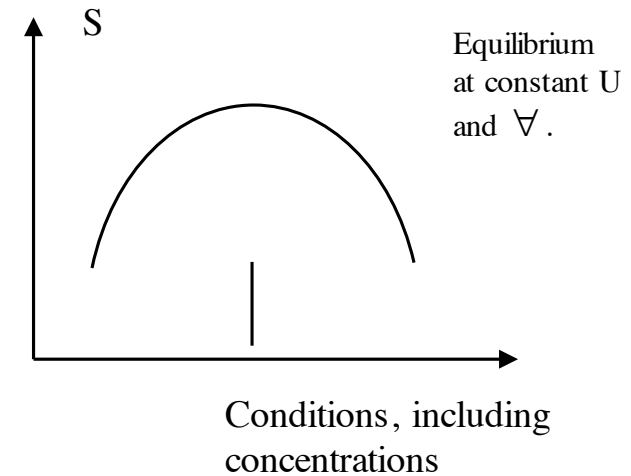
At constant (given) $(U, \forall): dS = dS_g$

and hence in terms of properties

$$dS \geq 0 \quad \text{at constant } (U, \forall)$$

$$S = \sum n_i \hat{s}_i (T, p_i), \quad p_i = X_i p$$

For a mixture undergoing a chemical reaction:

Mass transfer among the components maximizes S

S

Equilibrium
at constant U
and $\forall$.

Conditions, including
concentrations

Under different constraints, other conditions should be used:

$$H = U + p\forall$$

$$T\,dS_g = T\,dS - dH + \forall\,dp \geq 0 \rightarrow \quad \text{at constant } (p, H): \quad dS \geq 0$$

$$G = H - TS$$

$$TdS_g = -dG + \forall\,dp - S\,dT \geq 0 \rightarrow \text{at constant } (p, T): \quad dG \leq 0$$

$$A = U - TS$$

$$TdS_g = -dA - p\,d\forall - S\,dT \geq 0 \rightarrow \text{at constant } (T, \forall): \quad dA \leq 0$$

Maximizing (or minimizing a function (with mass conservation constraints) is used extensively in computer codes.

The Element Potential Method for Equilibrium Calculations

Maximize (or minimize) a function (with respect to the concentrations of the components) subject to constraints of Mass Conservation and two Thermodynamic properties (this approach is used in equilibrium computer codes)

e.g., for constant internal energy and volume, maximize the entropy,

$$S = \sum_N n_i \left[\hat{s}^o + \int_{T_o}^T \frac{\hat{c}_p(T)}{T} dT - \Re \left(\ell n \frac{p}{p_o} + \ell n X_i \right) \right] \rightarrow \text{max w.r.t. X}$$

subject to mass conservation and:

$$U = \sum_N n_i \hat{u}_i = \text{Constant}, \quad \forall = \sum_N n_i \hat{v}_i = \text{Constant}$$

It is best to use codes like CANTERA, CHEMKIN or EES.

Another Approach relies on *the Chemical Potential*

Gibbs Fundamental Relation With Mass Transfer

$$T\,dS = dU + p\,d\forall - \sum_N \mu_i dn_i$$

μ_i associated with change in S at constant U and $\forall$

as we change n_i by dn_i.   In finite form:

$$U = TS - p\forall + \sum_N \mu_i n_i,$$

Define Gibbs function again: $g = h - Ts,$

$$or \quad G = H - TS$$

$$G = U + p\forall - TS = \sum_N \mu_i n_i$$

But $G = \sum_N n_i \hat{g}_i,$ and hence $\mu_i = \hat{g}_i(T, p_i)$

For an Ideal Gas Mixture $\mu_i = \hat{g}_i(T, p_i) = \hat{g}_i^o(T) + \Re T \ell n\, p_i$

$$\mu_i = \hat{g}_i^o(T) + \Re T \ell n\, p + \Re T \ell n\, X_i,$$

where $\hat{g}^o(T) = \hat{g}^{oo} + \Im n(T),$

$\hat{g}^{oo}$ is standard Gibbs free energy (of formation)

Equilibrium in terms of Chemical Potential

The general expression of entropy generation with mass transfer

$$T\,dS_g = T\,dS - dU - p\,d\forall \quad (\geq 0 \text{ for equilibrium}),$$

combined with the Gibbs Fundamental relation:

$$T\,dS = dU + p\,d\forall - \sum_N \mu_i dn_i,$$

we get: $TdS_g = -\sum_N \mu_i dn_i,$ (entropy generation due to mass transfer)

and hence the general condition for mass transfer equilibrium

$$\sum_N \mu_i dn_i \leq 0$$

chemical potential drives mass transfer, similar to T driving heat transfer

and p driving work transfer (mass flux is proportional to $\nabla \mu$)

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The Equilibrium Constant of A Reaction

The conditon for equilibrium is:

$$\sum_{N} \mu_i dn_i = 0$$

When applied to the chemical reaction:

$$\sum_{react} v_i' \chi_i \Rightarrow \sum_{prod} v_i'' \chi_i,$$

For which ($v_i = v_i'' - v_i'$): $dn_i / v_i = \text{constant} = d\xi$

We get:

$$\sum_{species} v_i \mu_i = 0,$$

the Law of Mass Action

$$\sum_{prod} v_i'' \mu_i - \sum_{react} v_i' \mu_i = 0$$

The Equilibrium Constant of A Reaction

$$\sum_{prod} v_i'' \mu_i - \sum_{react} v_i' \mu_i = 0$$

with $\mu_i = \hat{g}_i(T, p_i) = \hat{g}_i^o(T) + \Re T \ln \dfrac{p_i}{p_o}$

$$\frac{\prod_{prod} p_i^{v_i''}}{\prod_{react} p_i^{v_i'}} = K_p(T), \quad p_o = 1 \text{ atm}, \ p_i \text{ in atm}$$

with the Equilibrium Constant

$$K_p(T) = \exp\left(-\frac{\Delta G_R^o(T)}{\Re T}\right)$$

$$\Delta G_R^o(T) = \sum_{prod} v_i'' \hat{g}_i^o(T) - \sum_{react} v_i' \hat{g}_i^o(T) = \sum_{species} v_i \hat{g}_i^o(T)$$

$\Delta G_R^o(T)$ is the Gibbs free energy of reaction @ T

it is a function of

the stoichiometric coefficients of the reaction and T

The equilibrium constant is defined as $K_P(T) = \dfrac{X_3^{v_3} X_4^{v_4}}{X_1^{v_1} X_2^{v_2}} \left(\dfrac{p}{p_o}\right)^{-v_1 - v_2 + v_3 + v_4}$

in which $P_O = 1$ atm: $v_1 A_1 + v_2 A_2 \Leftrightarrow v_3 A_3 + v_4 A_4$

table shows log K

| $H_2O \Leftrightarrow$ $OH + \frac{1}{2}H_2$	$\frac{1}{2}O_2 + \frac{1}{2}N_2 \Leftrightarrow$ NO	$CO_2 \Leftrightarrow$ $CO + \frac{1}{2}O_2$	$CO_2 + H_2 \Leftrightarrow$ $CO + H_2O$	T,K
-143.8	-46.453	-143.2	-19.6	100
-46.137	-15.171	-45.066	-5.018	298
-26.182	-8.783	-25.025	-2.139	500
-11.309	-4.062	-10.221	-0.159	1000
-8.811	-3.275	-7.764	+0.135	1200
-7.021	-2.712	-6.014	+0.333	1400
-5.677	-2.290	-4.706	+0.474	1600
-4.631	-1.962	-3.693	+0.577	1800
-3.793	-1.699	-2.884	+0.656	2000
-3.107	-1.484	-2.226	+0.716	2200
-2.535	-1.305	-1.679	+0.764	2400
-2.052	-1.154	-1.219	+0.802	2600
-1.637	-1.025	-0.825	0.833	2800
-1.278	-0.913	-0.485	+0.858	3000
-0.559	-0.69	+0.19	+0.902	3500
-0.022	-0.524	+0.692	+0.930	4000
+0.397	-0.397	+1.079	+0.946	4500
+0.731	-0.296	+1.386	+0.956	5000
+1.004	-0.214	+1.635	+0.960	5500
+1.232	-0.147	+1.841	+0.961	6000

Chemical reactions are algebraically additive:

$$R = R_1 + R_2 + R_3 \ldots$$

with $\Delta G_{R,1}^o$, $\Delta G_{R,2}^o$ ..... and $K_{p,1}$, $K_{p,2}$

$$\ell n K_p = -\frac{1}{\Re T}\left(\Delta G_R^o(T)\right)$$

$$= -\frac{1}{\Re T}\left(\Delta G_{R,1}^o(T) + \Delta G_{R,2}^o(T) + \Delta G_{R,3}^o(T) + \ldots\right)$$

$$= \ell n\left(K_{p,1}\right) + \ell n\left(K_{p,2}\right) + \ell n\left(K_{p,3}\right) + \ldots$$

$$= \ell n\left(K_{p,1} K_{p,2} K_{p,3} \ldots\right)$$

Example: Water Dissociation At High Temperature

1 mole of water becomes:

$$\left((1-\alpha) H_2O + \alpha H_2 + \frac{\alpha}{2} O_2 \right)$$

H_2O Equilibrium:
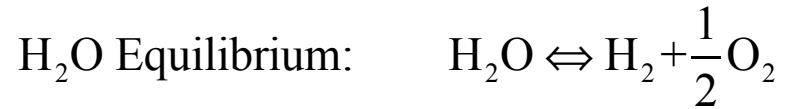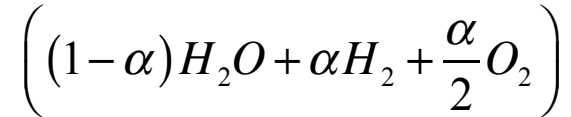
$$H_2O \Leftrightarrow H_2 + \frac{1}{2} O_2$$

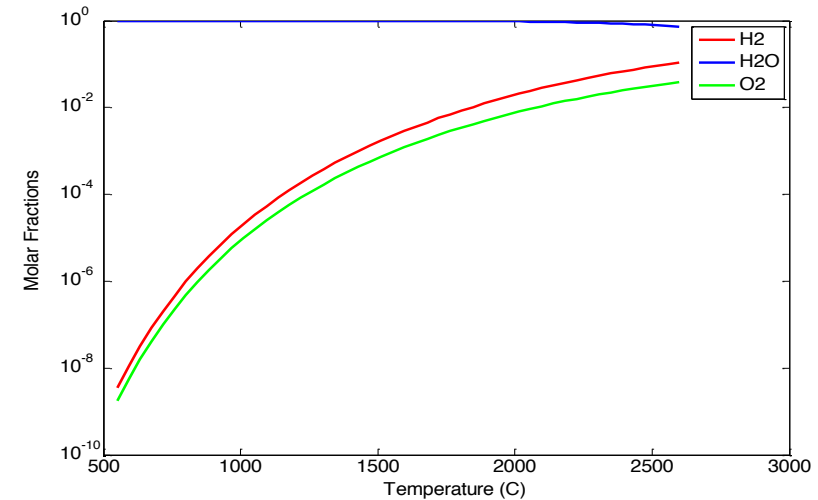mole fractions: $n_{total} = \sum_{mixture} \alpha_i, \quad X_i = \frac{\alpha_i}{n_{total}}$

$$\frac{X_{H_2} X_{O_2}^{1/2}}{X_{H_2O}} = \frac{K_{p,H_2O}}{\sqrt{p}},$$

$$K_{p,H_2O \to H_2 + \frac{1}{2}O_2}(T) = \exp\left(-\frac{\Delta G^o_{R,H_2O}(T)}{\Re T} \right)$$

$$\frac{\alpha}{1-\alpha} \left(\frac{\alpha}{2+\alpha} \right)^{1/2} = \frac{K_{p,H_2O}}{\sqrt{p}}$$

at 3000 K, $X_{H_2O} = 0.794$, $X_{H_2} = 0.137$, and $X_{O_2} = 0.069$.

Equilibrium limitation for water splitting

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Temperature Dependence of Equilibrium Composition

The van't Hoff Equation:
$$\frac{d\left(\ell n\, K_p\right)}{d\left(1/T\right)} = -\frac{\Delta H_R}{\Re}$$

and
$$K_p \approx \bar{K}_p^o \exp\left(-\frac{\Delta H_R^0}{\Re T}\right)$$

- The "partial pressure" of a solid is one.
- The reverse reaction has the inverse equilibrium constant.
- Additive reactions have multiplicative equilibrium constant.

Exothermic reactions

$$CO + \frac{1}{2}O_2 \xrightarrow{R1} CO_2 \qquad \frac{X_{CO_2}}{X_{CO}X_{O_2}^{1/2}} = \sqrt{p}\, K_{p,R1}$$

or $H_2 + \frac{1}{2}O_2 \xrightarrow{R2} H_2O \qquad \frac{X_{H_2O}}{X_{\_\_}X_{\_}^{1/2}} = \sqrt{p}\, K_{p,R2},$

Endothermic reaction
$N_2 + O_2 \rightarrow 2NO$

K_p (vertical axis), T (horizontal axis)

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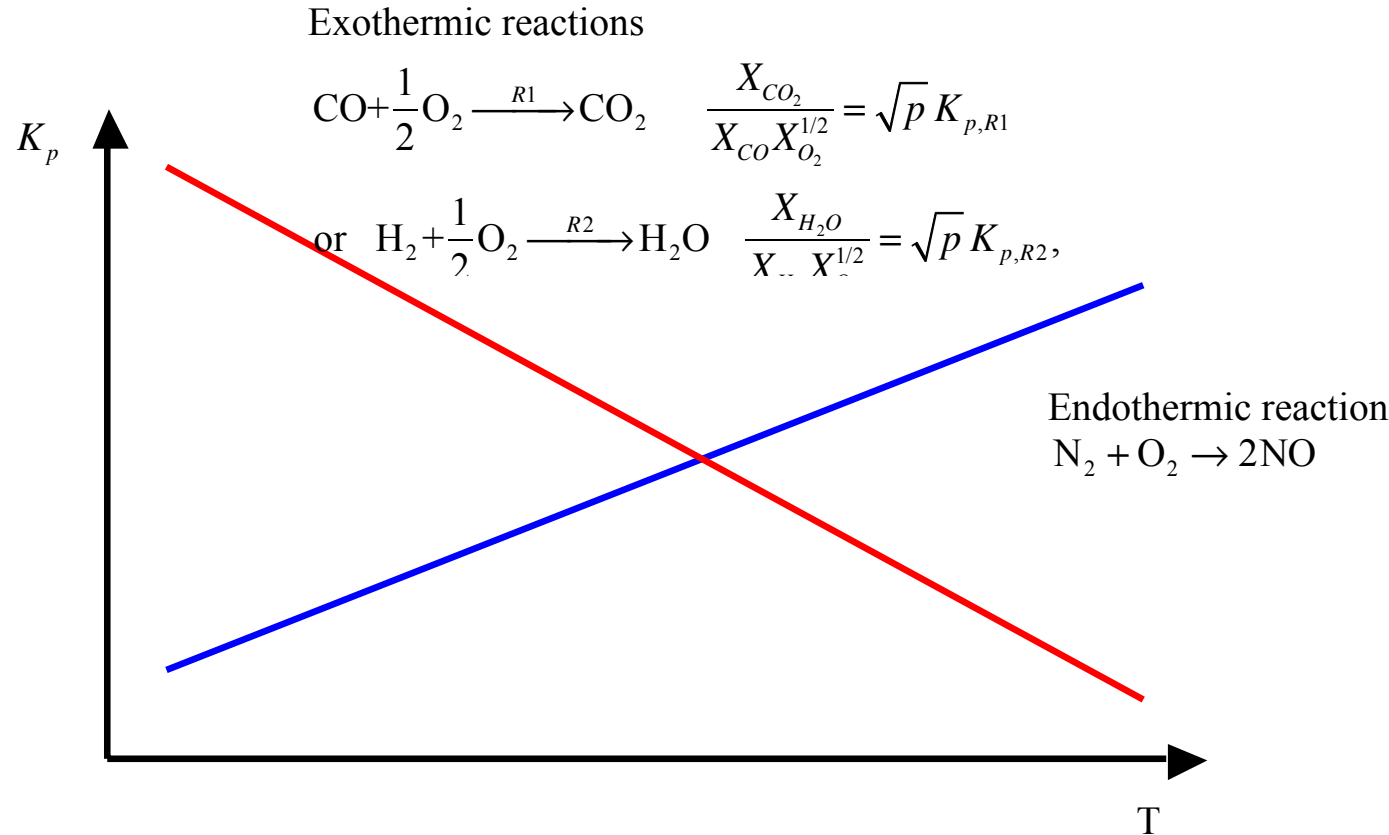
Example: CO_2 reduction to CO at high T

Q

CO$_2$ @ 298 K and 6 atm

exit @ 2800 and 5 atm

Heating CO2 from 298 K to 2800 K, while p drops:

mass conservation: mixture is $\left((1-\alpha)CO_2 + \alpha CO + \dfrac{\alpha}{2}O_2 \right)$,

$$n_{total} = \sum_{mixture} \alpha_i, \quad X_i = \frac{\alpha_i}{n_p}$$

CO_2 Equilibrium: $CO_2 \Leftrightarrow CO + \dfrac{1}{2}O_2$, $\quad \dfrac{X_{CO}X_{O_2}^{1/2}}{X_{CO_2}} = \dfrac{K_{p,CO_2}}{p^{1/2}}$,
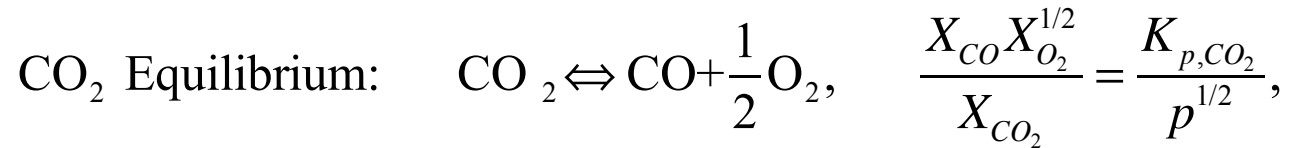
$$\frac{K_p^2}{p} = \frac{\alpha^3}{(1-\alpha)^2(2+\alpha)}$$

@ 2800K, $\alpha = 0.1867$, or 18.7% carbon dioxide dissociation.

how much thermal energy is needed:

Energy Conservation: $\quad Q = \left[(1-\alpha)\hat{h}_{co_2}^{2800} + \alpha\hat{h}_{CO}^{2800} + \dfrac{\alpha}{2}\hat{h}_{o_2}^{2800} \right] - \hat{h}_{CO_2}^{298}$.

and $Q = 192$ MJ/kmolCO$_2$. If dissociation was neglected, $Q = 140$ MJ/kmolCO$_2$
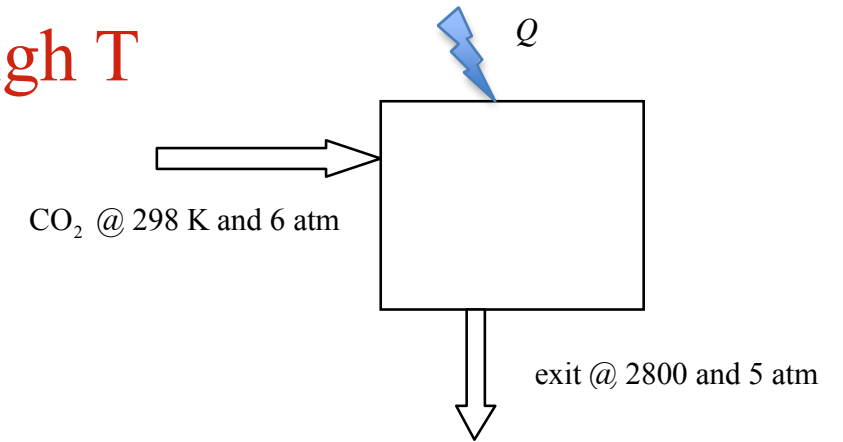
Equilibrium limitation for CO$_2$ reduction

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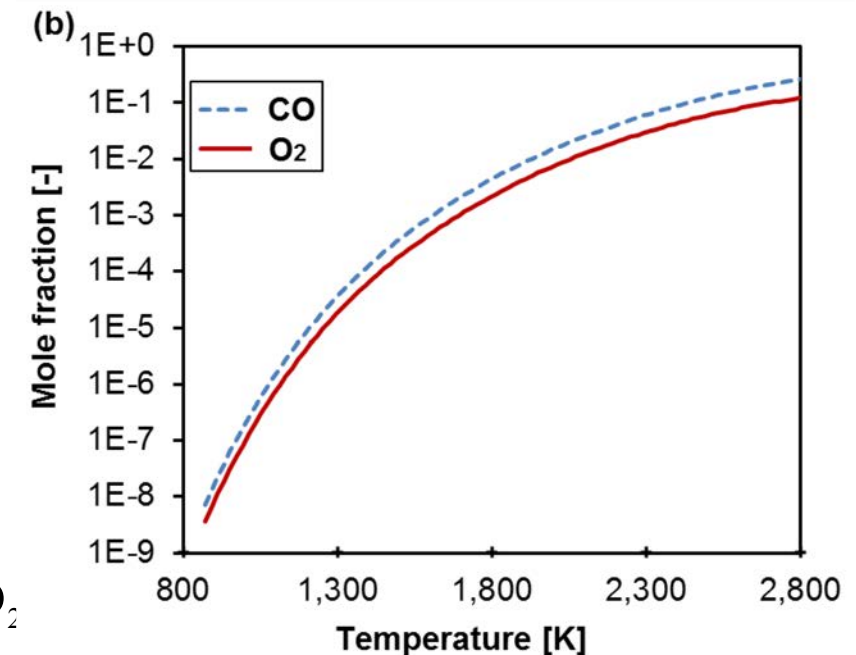
Pressure Dependence of Equilibrium Composition

$$\frac{\prod\limits_{prod} X_i^{v_i''}}{\prod\limits_{react} X_i^{v_i'}} = \frac{K_p(T)}{p^\sigma} \quad \text{where} \quad \sigma = \sum_{prod} v_i'' - \sum_{react} v_i'$$

Complete oxidation of coal: $C + O_2 \rightarrow CO_2$ is pressure independent.

Partial Oxidation: $C + \frac{1}{2}O_2 \rightarrow CO$ favors reactants at high p

$$\frac{X_{CO}}{X_{O_2}} = \frac{K_{p,C+\frac{1}{2}O_2\rightarrow CO}(T)}{\sqrt{p}}$$

So does steam reforming of coal: $C + H_2O \rightarrow CO + H_2$

$$\frac{X_{CO}X_{H_2}}{X_{H_2O}} = \frac{K_{p,C+H_2O\rightarrow CO+H_2}(T)}{p}$$

Example 3.9. Formation of NO in hot Air

When heated, air may partially dissociate and yield NO. Assume air is made up of 21% of O_2 and 79% of N_2. Consider the dissociation of air at 1500 and 2000 K at 1 atmosphere. Determine the concentration of NO at these two conditions.

Solution:

The equilibrium reaction for the dissociation of NO from O_2 and N_2 is: $N_2 + O_2 \Leftrightarrow 2\,NO$. We can alternatively choose the equilibrium reaction, which corresponds to NO formation: $1/2\,N_2 + 1/2\,O_2 \Leftrightarrow NO$. We will use the first equilibrium reaction to show how one can relate the equilibrium constant of this reaction to that of the formation reaction. The actual global reactions relating air (the reactants) and its products (air and dissociation of air) may be written, per mole of O_2 in air, as: $O_2 + 3.76\,N_2 \Leftrightarrow a\,O_2 + b\,N_2 + c\,NO$. The atom balance yields 2 equations for the elements N and O:

O: $\qquad 2 = 2a + c$

N: $\qquad 3.76 \times 2 = 2b + c$

However, we have 3 unknowns, a, b and c, and an additional equation is needed to find all of them. This equation will be based on the equilibrium reaction $N_2 + O_2 \Leftrightarrow 2\,NO$ whose rate constant can be related to the partial pressures of the species in the products of the global reaction:

$$K_p(T) = \frac{p_{NO}^2}{p_{N_2} p_{O_2}} = \frac{X_{NO}^2 p^2}{\left(X_{N_2} p\right)\left(X_{O_2} p\right)} = \frac{X_{NO}^2}{X_{N_2} X_{O_2}}.$$

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The mole fractions are expressed as: $X_{O_2} = \dfrac{a}{a+b+c}$, $X_{N_2} = \dfrac{b}{a+b+c}$, $X_{NO} = \dfrac{c}{a+b+c}$, which after substitution of b and c in terms of a from the above elemental balance yields:

$$X_{O_2} = \frac{a}{4.76}, \quad X_{N_2} = \frac{2.76+a}{4.76}, \quad X_{NO} = \frac{2(1-a)}{4.76}.$$

Substituting these mole fractions into the expression for the equilibrium constant above yields:

$$K_p(T) = \frac{4(1-a)^2}{a(2.76+a)}.$$

We can formulate the expression for the unknown a in terms of a quadratic equation:

$$(4-K_p)a^2 - (8+2.76K_p)a + 4 = 0$$

with the only valid root for a that corresponds to a positive value. The equilibrium constants at 1500 K and 2000 K are: 1.0617×10^{-5} and 3.9945×10^{-4}, respectively. Increasing the equilibrium constant between 1500 and 2000 K indicates a higher amount of dissociation of heated air at the higher temperature.

Solving the above quadratic equation at 1500 K gives a = 0.997, b = 3.769 and c = 6.306x10^{-3}. On the other hand, at 2000 K, we get a = 0.981, b = 3.741 and c = 3.831 x10^{-3}. Thus, the concentration of NO at 1500 K and 2000 K is 0.13% and 0.8%, respectively.

Methane-steam Reforming for Hydrogen production

$$CH_4 + H_2O \Rightarrow CO + 3H_2, \quad \Delta H_R^o = 206.4 \text{ kJ/gmol} - \text{methane}$$

Start with one mole of methane and one mole of water

Determine the equilibrium of Mixture: $(CH_4, CO, CO_2, H_2, H_2O)$

3 mass conservations, and two equilibrium:
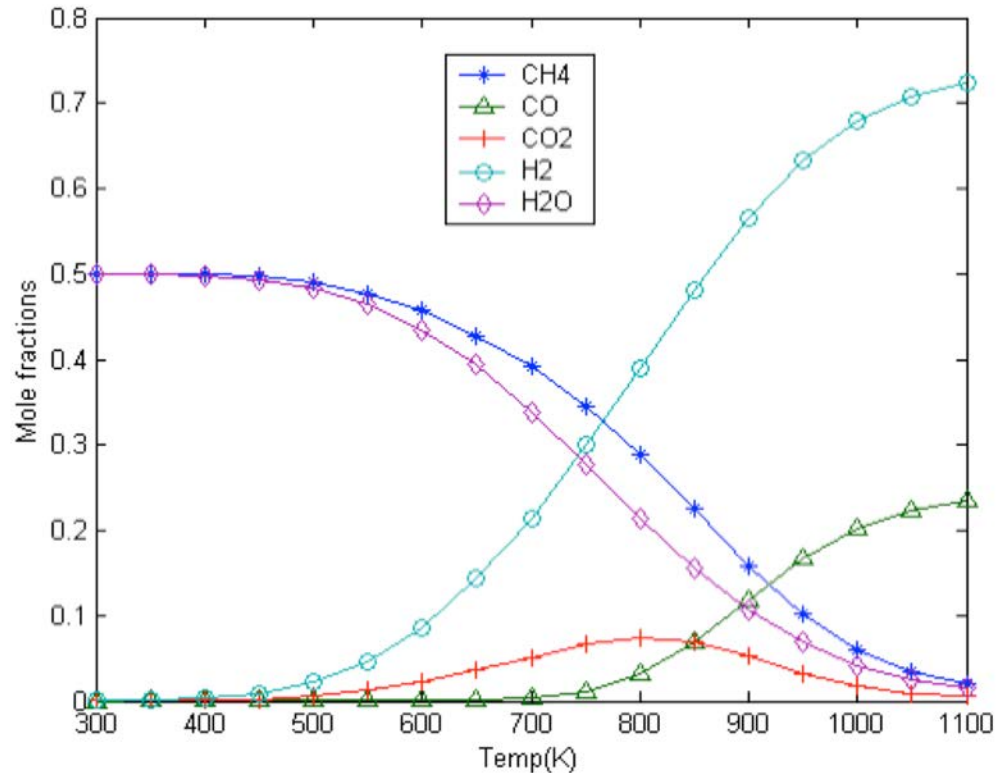
- Run at high T to maximize H_2 yield (equilibrium shift).
- Works better (shift towards H_2) at lower p.
- Needs catalysis (to speed up kinetics) even at these T.
- More endothermic at higher T.
- Fast quench (sudden drop in T) can freeze the mixture composition.

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Water-Gas Shift to remove CO and increase H_2 concentration

$$H_2O + CO \Rightarrow H_2 + CO_2, \quad \Delta H_R^o = -42\,\text{kJ/gmolCO}$$
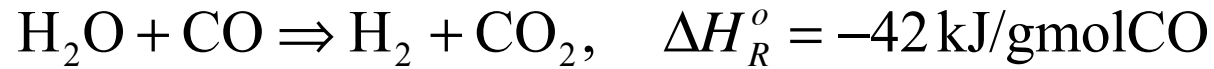
$\left(\text{start with equal volumes of CO, } CO_2, H_2 \text{ and } H_2O \text{ @ 1100 K}\right)$
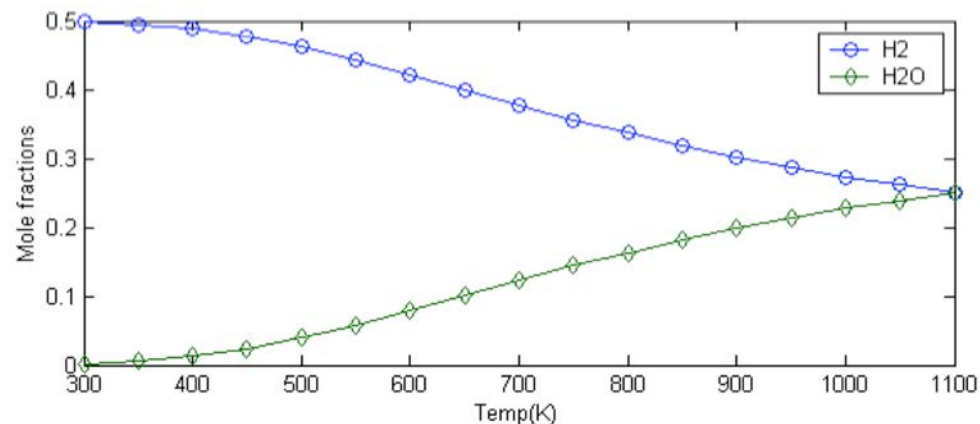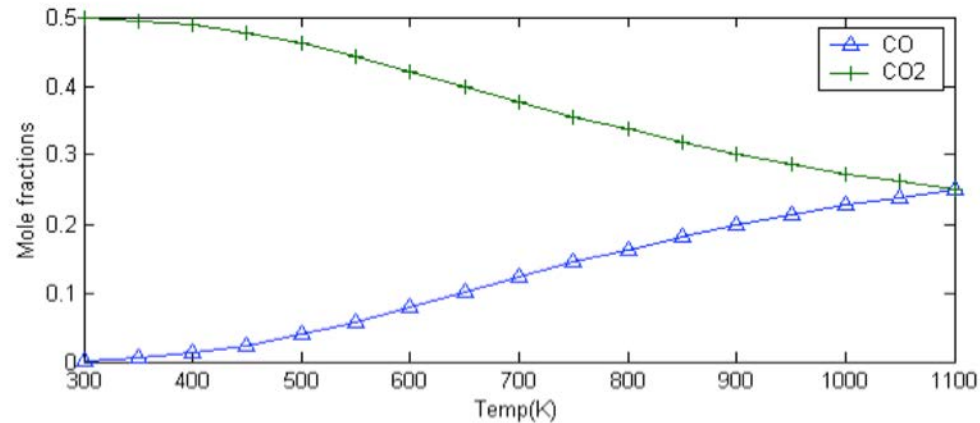
- Weakly endothermic at higher T (water in liquid phase).
- Should run at low T to maximize H_2 yield, two steps are often used (keep kinetics fast at high T).
- Need a catalyst to speed up the reactions (nickel and copper).
- Heat should be recycled to improve efficiency.

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Application: Hydrogen Production by Steam Reforming
Define reactor conditions to achieve maximum conversion
Temperature must be raised to shift equilibrium away from methane, then lowered to shift equilibrium towards hydrogen

Steam Reforming
$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$
$$\Delta h = 206.3 \text{ kJ/mol CH}_4$$
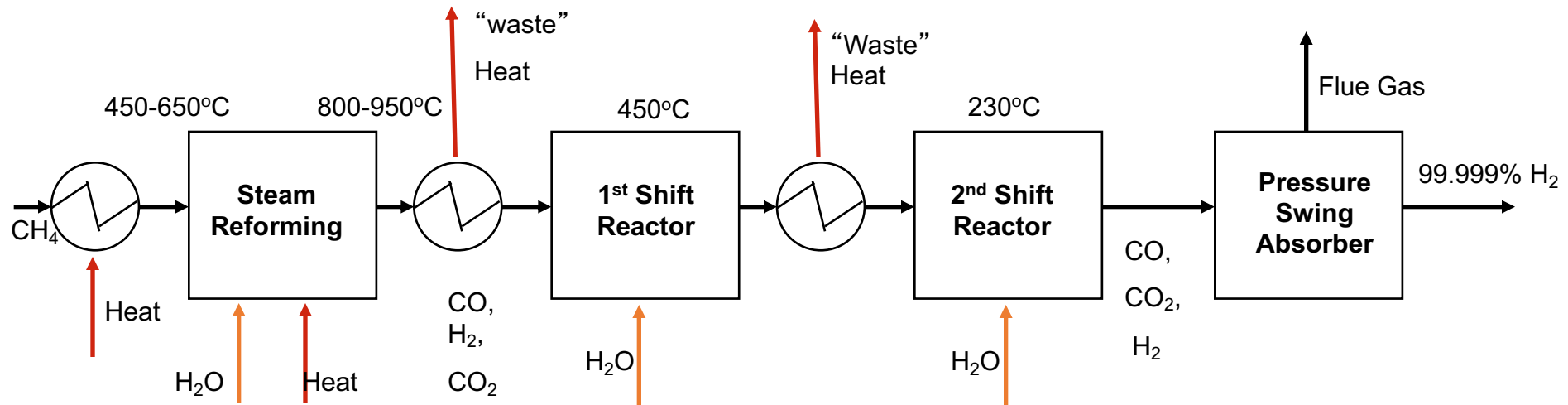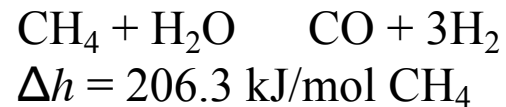
Water Gas Shift Reaction
$$CO + H_2O \rightleftharpoons CO_2 + H_2$$
$$\Delta h = -41.19 \text{ kJ/mol CO}$$
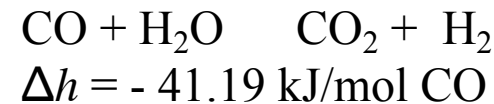
Max Efficiency = 85% if some "waste heat" can be used internally

Efficiency = 60 to 70% for on-site reforming, up to 85% with integration

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A Practical Scheme for Methane Reforming
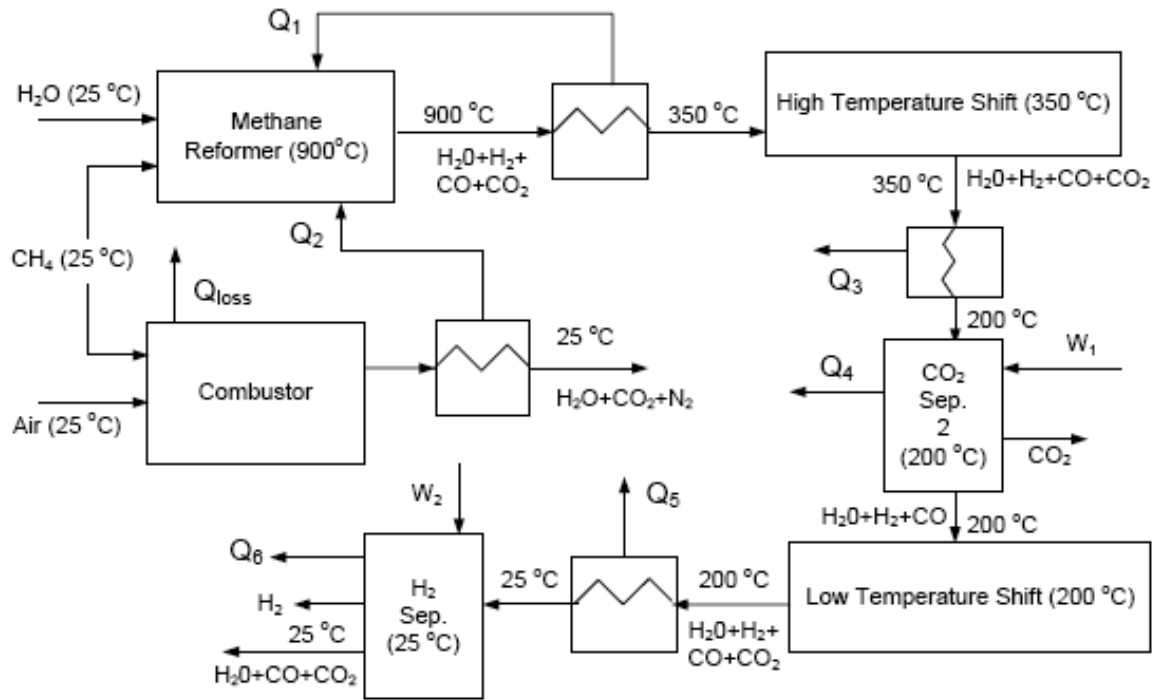
Hydrogen
Worldwide production and cost based on SMR
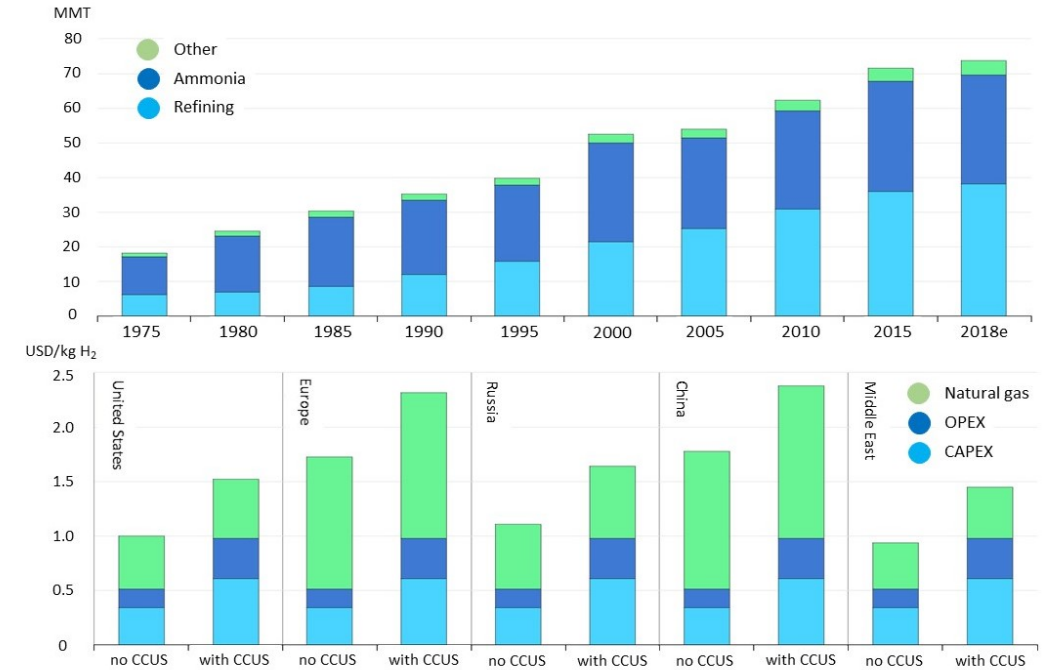
IEA Technology Report, June 2019,
https://www.iea.org/reports/the-future-of-hydrogen.

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Methane (dry) reforming in CO_2

$$CH_4 + CO_2 \rightleftarrows 2CO + 2H_2 \qquad \Delta H_R^o = 246 \text{ kJ/mol}$$
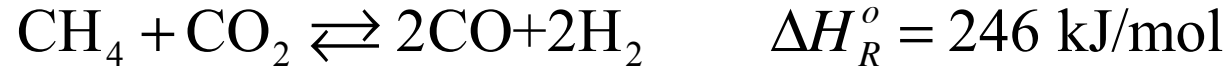
allowing for the co-existence of CH_4, CO_2, CO, H_2, O_2, and H_2O

Minimize Gibbs free energy .

Staring with 6% methane in CO2 at 300 K
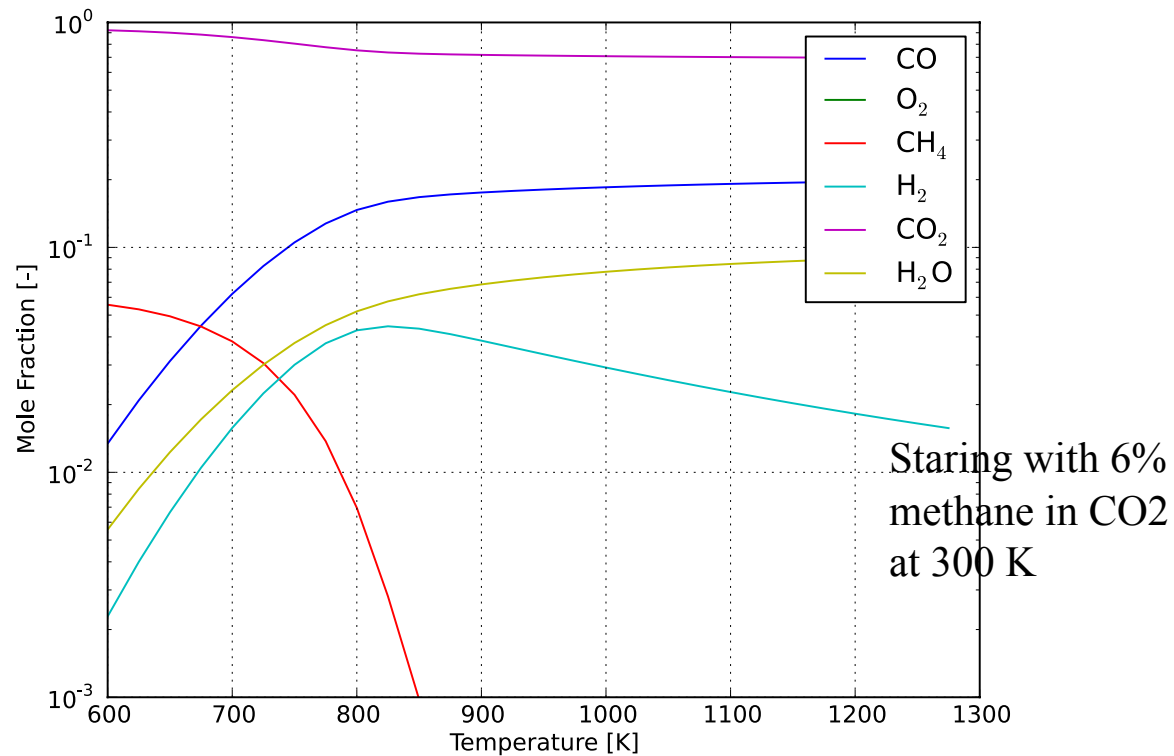
- Proposed for the generation of Solar Fuels, and /or recycling CO_2.
- The syngas stores the solar energy in chemical bonds.
- If products are continuously removed, the equilibrium can be shifted towards more products.
- Significant fraction of "dead" products: H_2O and CO_2

Or impose equilibrium of the reforming reaction + the water-gas shift (without O_2) + 3 conservation equations.

Direct Irradiation Systems

Elysia Sheu's
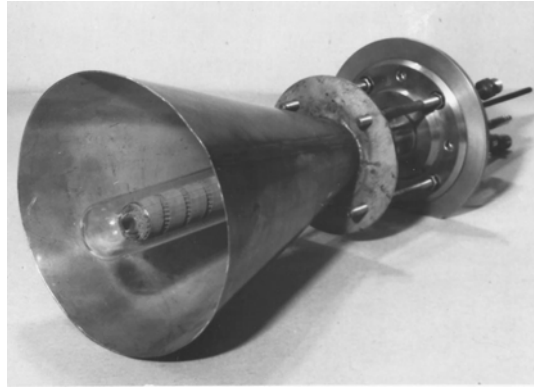
Anikeev et al. *Solar Energy,* 1998

Buck et al. *Solar Energy Materials,* 1991

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- Two main components:
  - Solar receiver
  - Chemical reactor
    - Absorber matrix
- Typically reaction rate limited
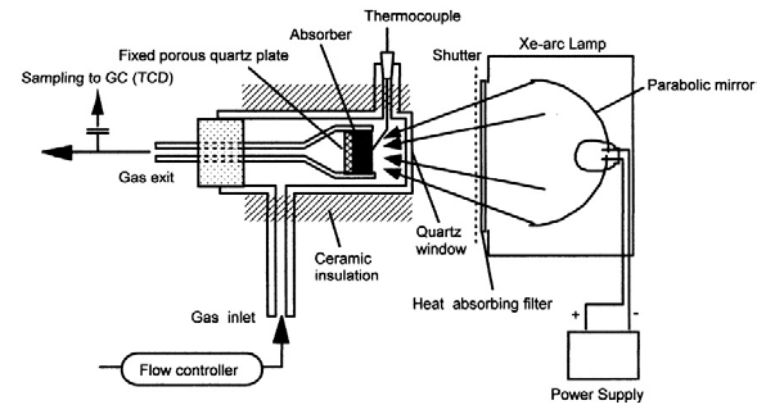
Kodama et al. *Energy & Fuels,* 2003

Because of the number of heat transfer processes, system integration is very important for raising the overall reforming efficiency …

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

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

A number of high efficiency heat exchangers are needed …
Cost is a concern, perhaps more justifiable for large production facility.
Less so for local operation or mobile applications ..
Progress and innovation ARE underway …

How to beat equilibrium limitations?

Continuously remove the products (one or both) from the mixture. An ion transport membrane can remove O_2 at T (750-1000 C)

H_2O splitting: $H_2O \Leftrightarrow H_2 + \dfrac{1}{2}O_2$, $\quad \dfrac{X_{H_2}}{X_{H_2O}} = \dfrac{K_{p,H_2O}}{X_{O_2}^{1/2}\sqrt{p}}$,
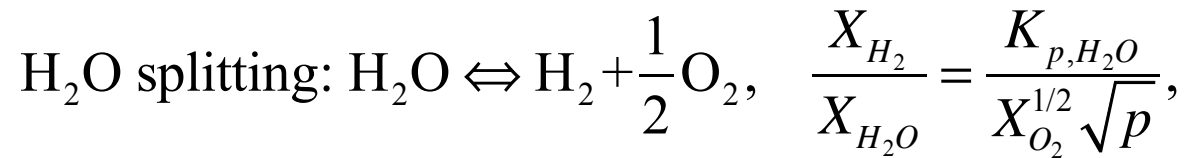
Thus, by removing O_2 (across a membrane) and reducing its mole fraction in the mixture,

the equation shows X_{H_2} will increase, removing oxygen encourages more dissociation of water.

H_2O/CO_2

H_2/CO

O_2
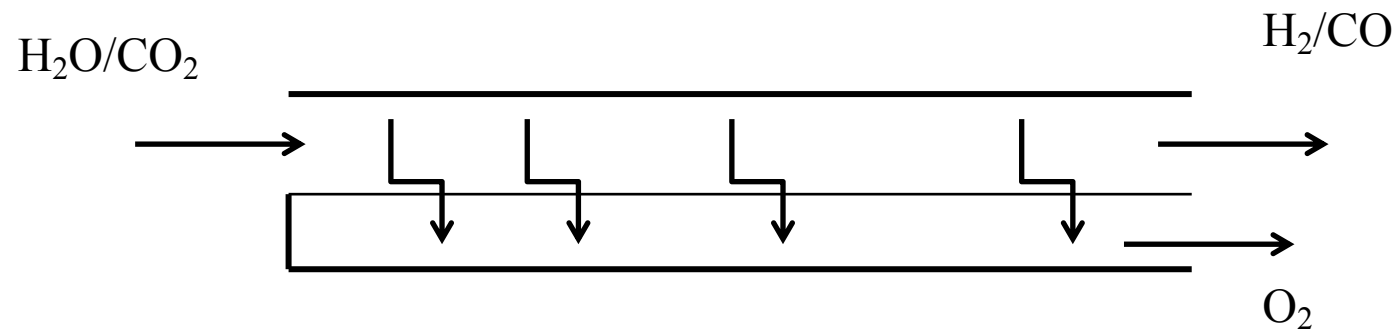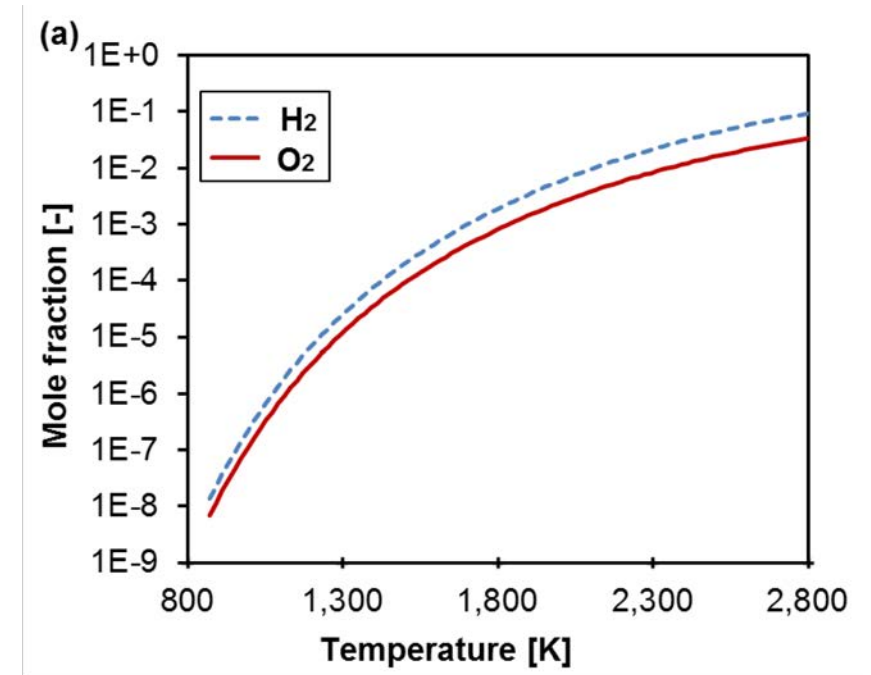
$p_{feed} \gg p_{sweep}$

$$J_{O_2} \approx A\, e^{E_a/\Re T}\left(\sqrt{p_{O_2,feed}} - \sqrt{p_{O_2,sweep}}\right)$$

23

Projects …

Induction Heating of Firebrick for Electricity-to-High-Temperature Stored Heat for Industry and Power

R. T. Ibekwe, C. W. Forsberg, A. F. Ghoniem
Massachusetts Institute of Technology
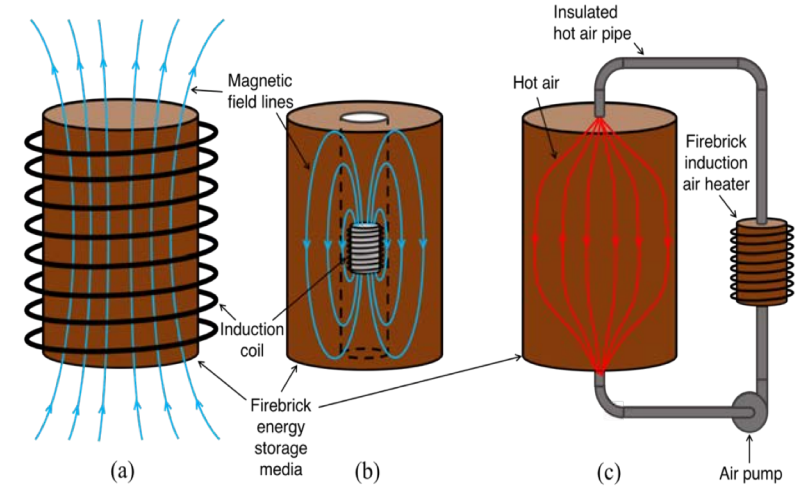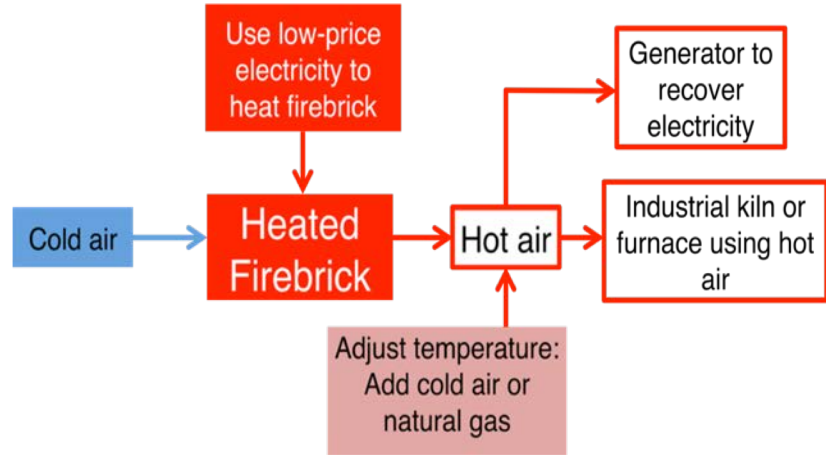

Schematic diagram of a firebrick energy storage system

Three proposed design concepts for an induction-heated firebrick energy storage system. Concept (a) is the one investigated in this work.
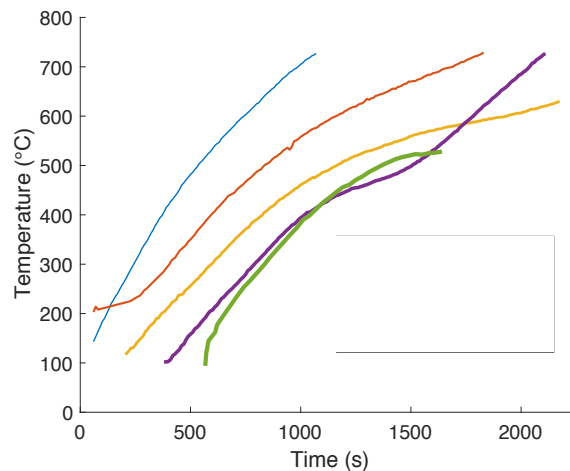
Plots of temperature against time for various firebricks under induction heating.

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Cold-Side Thermal Energy Storage for Dry-Cooled Concentrating Solar Power Plants
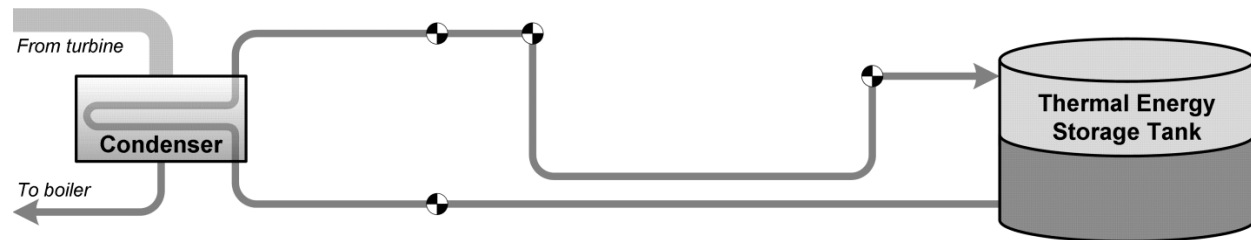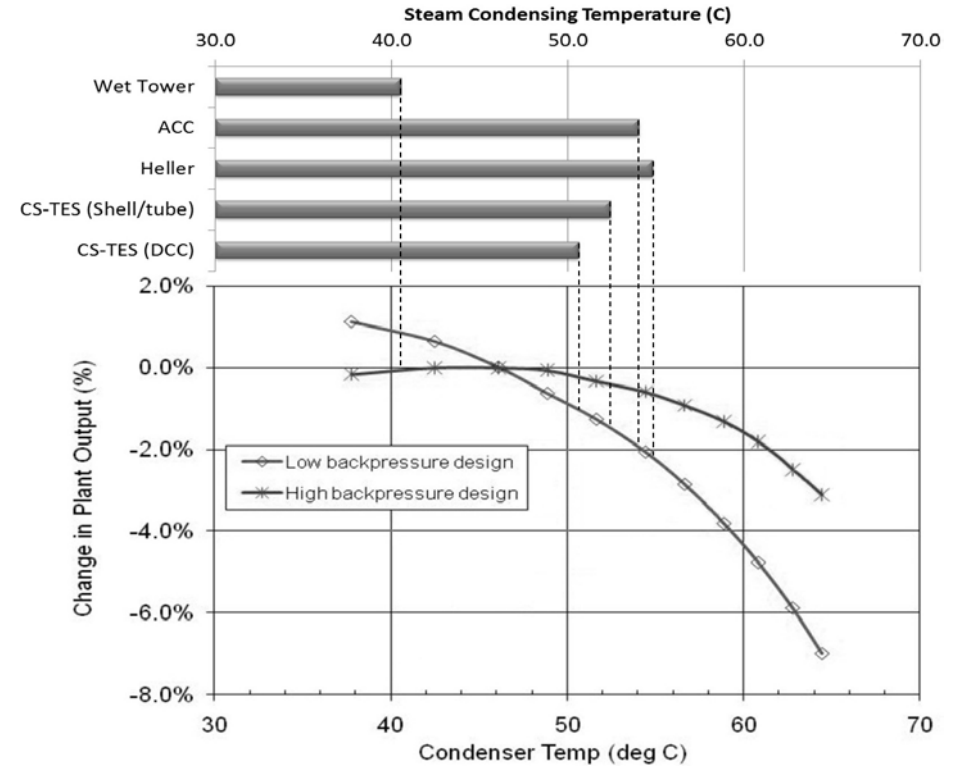
Michael J. Rutberg and Ahmed F. Ghoniem
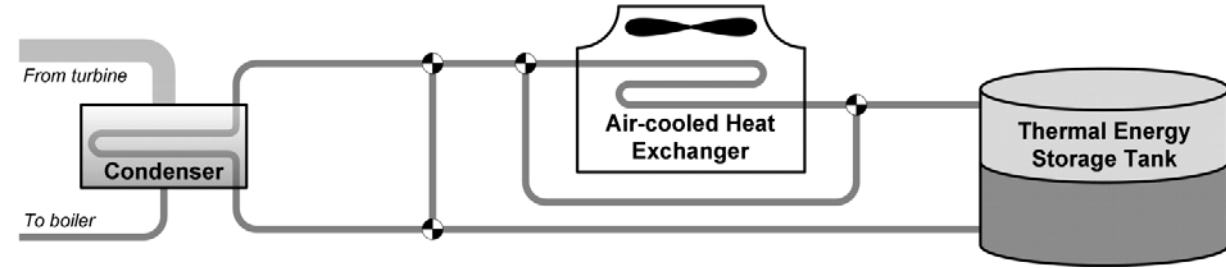
The cold-side thermal energy storage (CS-TES) cooling system architecture
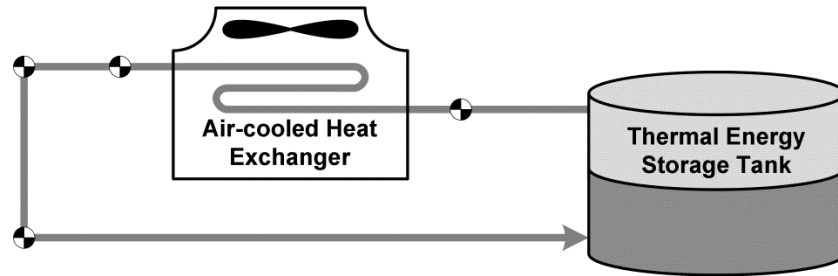
CS-TES operational mode: Overnight cooling

CS-TES operational mode: Daytime operation

Case study steam condensing temperatures, optimized with NPV of cooling system costs constant at $41m (except wet tower: $13m); typical turbine output curves (Turchi et al., 2010) are shown for reference

Next-generation HVAC: Prospects for and limitations of desiccant and membrane-based dehumidification and cooling

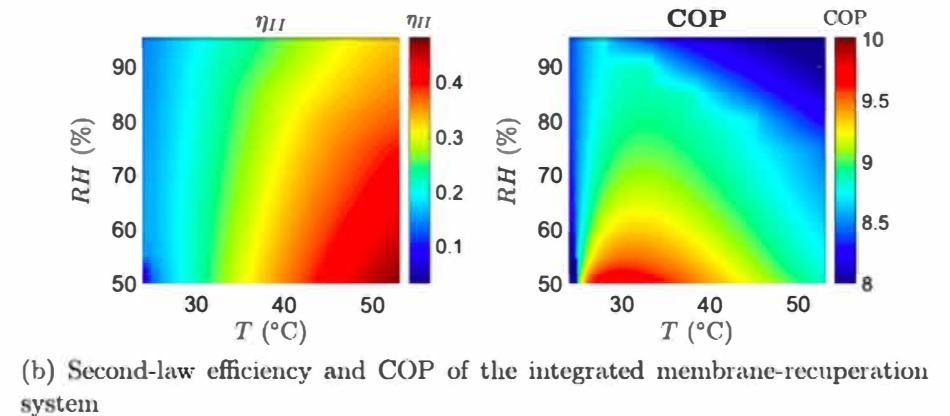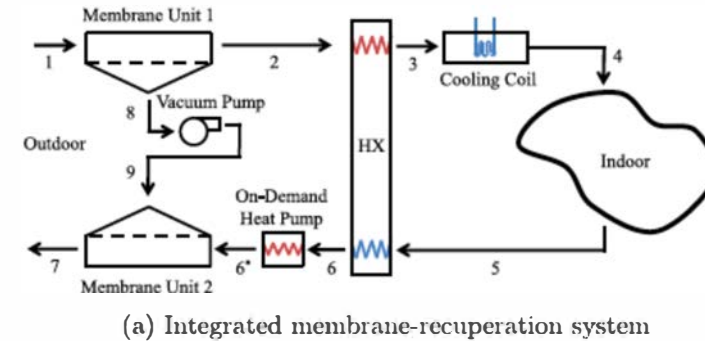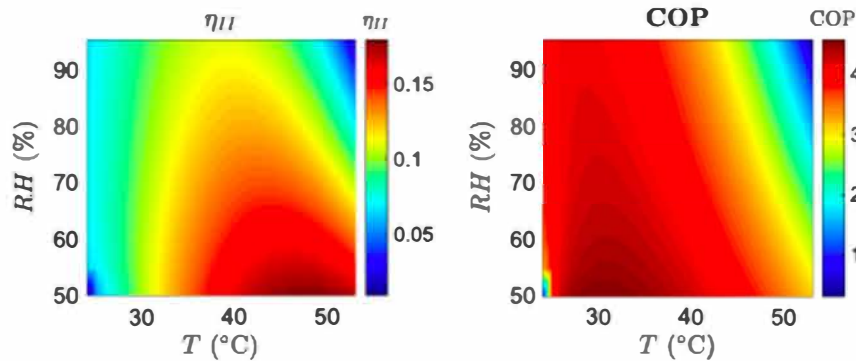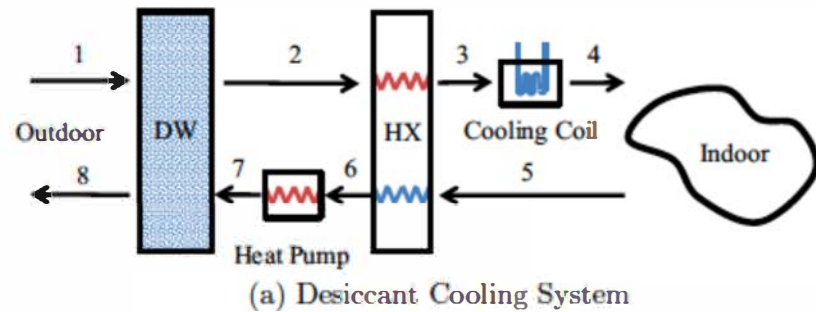Omar Labban [a,1], Tianyi Chen [a,1], Ahmed F. Ghoniem [a,2], John H. Lienhard V [a,2], Leslie K. Norford [b,*,2]

(a) Desiccant Cooling System

(b) Efficiency of the DCS with cooling coil system

(a) Integrated membrane-recuperation system

(b) Second-law efficiency and COP of the integrated membrane-recuperation system

Fig. 11. Performance of the integrated membrane-recuperation system.

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2.60J Fundamentals of Advanced Energy Conversion
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