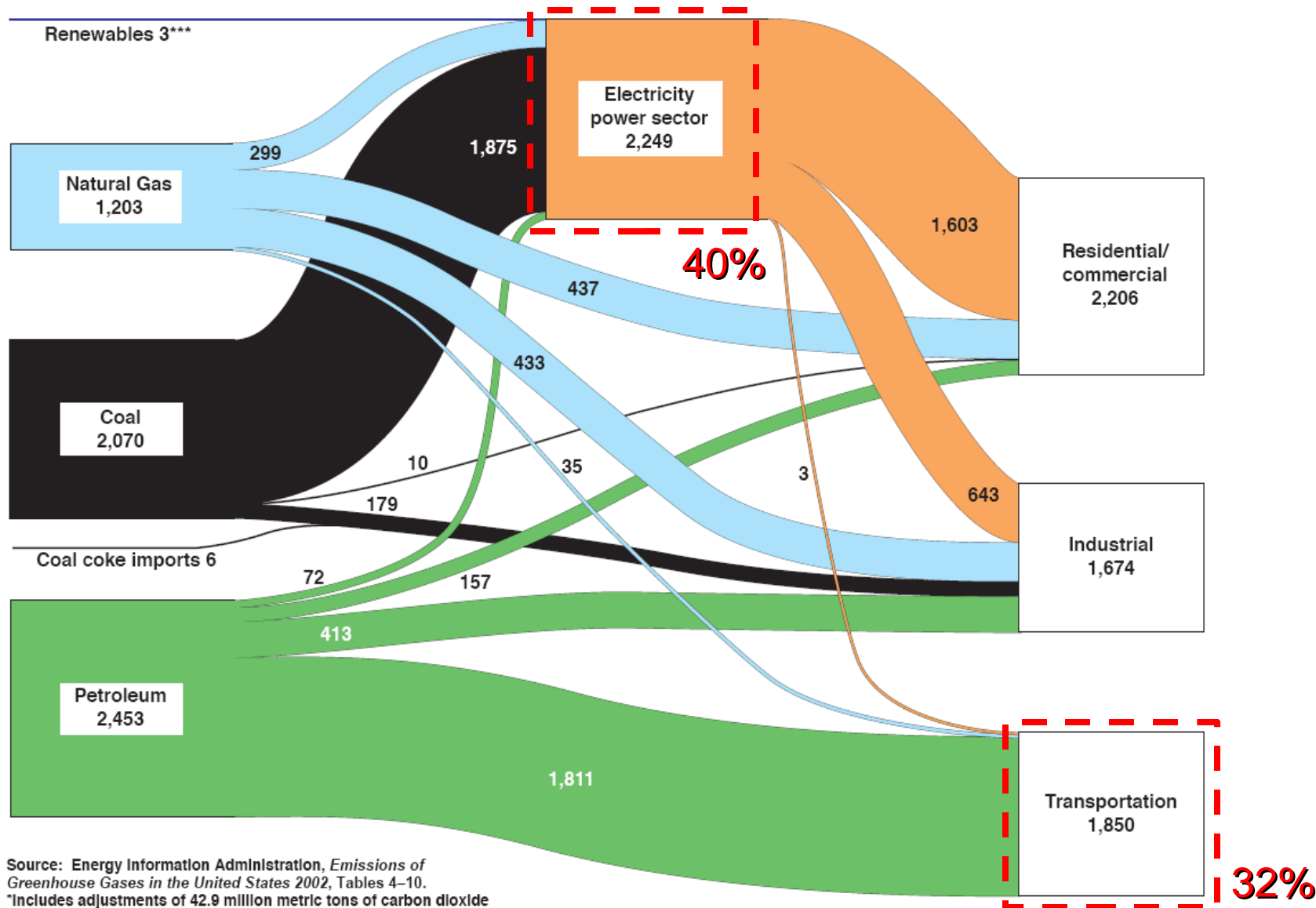




# Prospects for the Development of High-Efficiency, Low-Irreversibility Engines

C.F. Edwards,

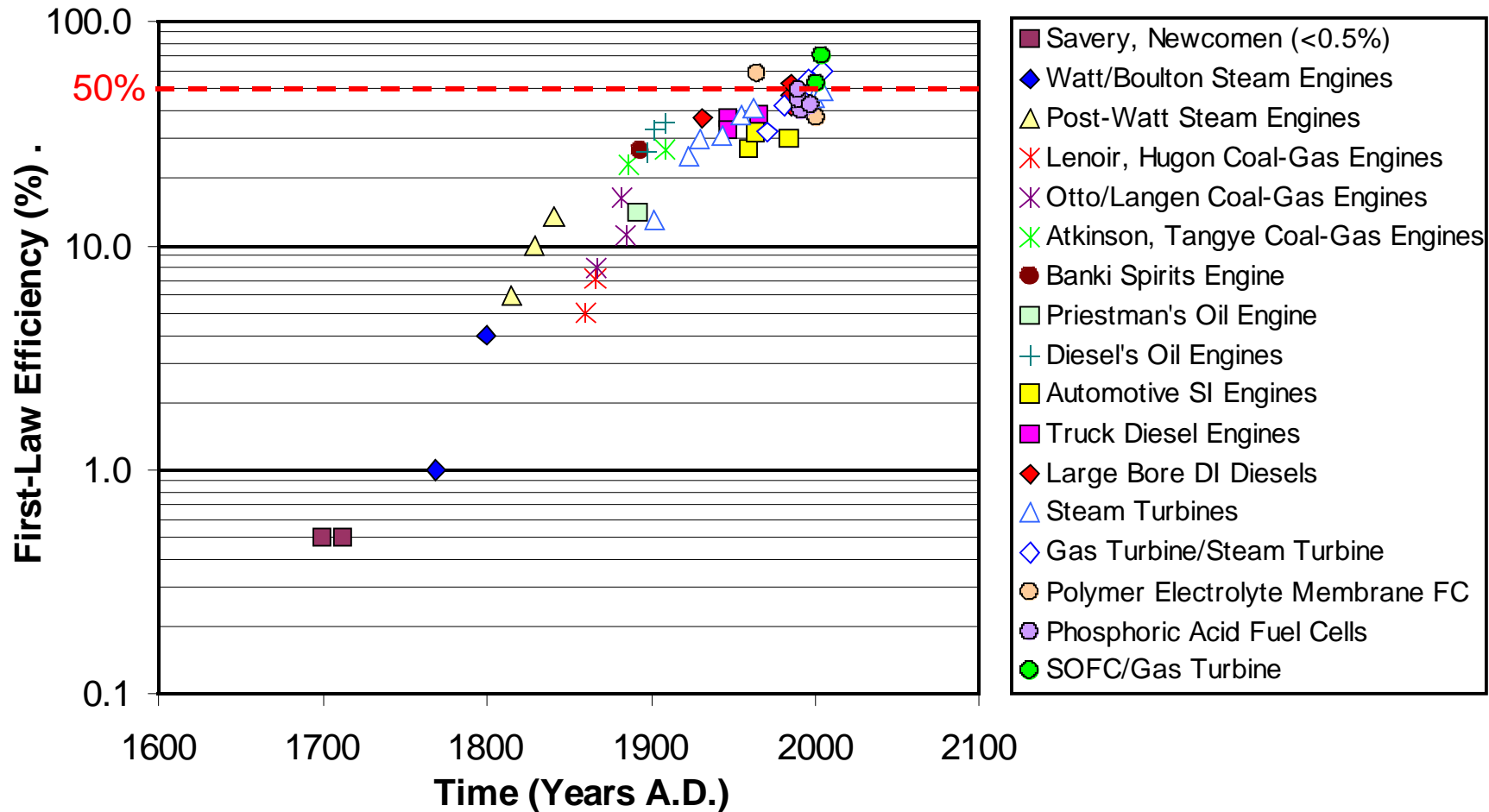
# U.S. 2002 Carbon Dioxide Emissions from Energy Consumption – 5,682\* Million Metric Tons of CO<sub>2</sub>\*\*



Source: Energy Information Administration, *Emissions of Greenhouse Gases in the United States 2002*, Tables 4–10.  
 \*Includes adjustments of 42.9 million metric tons of carbon dioxide from U.S. territories, less 90.2 MtCO<sub>2</sub> from international and military bunker fuels.  
 \*\*Previous versions of this chart showed emissions in metric tons of carbon, not of CO<sub>2</sub>.  
 \*\*\*Municipal solid waste and geothermal energy.  
 Note: Numbers may not equal sum of components because of independent rounding.

Lawrence Livermore National Laboratory, May 2004  
<http://eed.llnl.gov/flow/>

# Conversion Efficiency of “Engines”



# Chemical Exergy of Common Fuels

Fuel Species+	Chemical Formula	Chem. Exergy <sup>†</sup>		$\Delta H^\circ$ Reaction*		$\Delta G^\circ$ Reaction*		$\Delta S^\circ$ Reaction*		Exergy to LHV Ratio
		MJ per fuel kmol	kg	MJ per fuel kmol	kg	MJ per fuel kmol	kg	kJ/K per fuel kmol	kg	
Methane	CH <sub>4</sub>	832	51.9	-803	-50.0	-801	-49.9	-5.2	-0.33	1.037
Methanol	CH <sub>3</sub> OH	722	22.5	-676	-21.1	-691	-21.6	50.4	1.57	1.068
Carbon Monoxide	CO	275	9.8	-283	-10.1	-254	-9.1	-98.2	-3.51	0.971
Acetylene	C <sub>2</sub> H <sub>2</sub>	1267	48.7	-1257	-48.3	-1226	-47.1	-104.6	-4.02	1.008
Ethylene	C <sub>2</sub> H <sub>4</sub>	1361	48.5	-1323	-47.2	-1316	-46.9	-25.2	-0.90	1.029
Ethane	C <sub>2</sub> H <sub>6</sub>	1497	49.8	-1429	-47.5	-1447	-48.1	60.5	2.01	1.048
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	1363	29.6	-1278	-27.7	-1313	-28.5	117.7	2.56	1.067
Propylene	C <sub>3</sub> H <sub>6</sub>	2001	47.6	-1926	-45.8	-1937	-46.0	36.6	0.87	1.039
Propane	C <sub>3</sub> H <sub>8</sub>	2151	48.8	-2043	-46.3	-2082	-47.2	129.2	2.93	1.053
Butadiene	C <sub>4</sub> H <sub>6</sub>	2500	46.2	-2410	-44.5	-2421	-44.7	36.9	0.68	1.038
i-Butene	C <sub>4</sub> H <sub>8</sub>	2644	47.1	-2524	-45.0	-2560	-45.6	120.2	2.14	1.047
i-Butane	C <sub>4</sub> H <sub>10</sub>	2800	48.2	-2648	-45.6	-2712	-46.7	214.4	3.69	1.058
n-Butane	C <sub>4</sub> H <sub>10</sub>	2805	48.3	-2657	-45.7	-2717	-46.7	200.0	3.44	1.056
n-Pentane	C <sub>5</sub> H <sub>12</sub>	3460	48.0	-3272	-45.3	-3353	-46.5	271.3	3.76	1.057
i-Pentane	C <sub>5</sub> H <sub>12</sub>	3454	47.9	-3265	-45.2	-3347	-46.4	277.0	3.84	1.058
Benzene	C <sub>6</sub> H <sub>6</sub>	3299	42.2	-3169	-40.6	-3190	-40.8	69.4	0.89	1.041
n-Heptane	C <sub>7</sub> H <sub>16</sub>	4769	47.6	-4501	-44.9	-4625	-46.2	415.0	4.14	1.060
i-Octane	C <sub>8</sub> H <sub>18</sub>	5422	47.5	-5100	-44.7	-5259	-46.0	531.4	4.65	1.063
n-Octane	C <sub>8</sub> H <sub>18</sub>	5424	47.5	-5116	-44.8	-5261	-46.1	487.1	4.26	1.060
Jet -A	C <sub>12</sub> H <sub>23</sub>	7670	45.8	-7253	-43.4	-7440	-44.5	626.4	3.74	1.057
Hydrogen	H <sub>2</sub>	236	117.2	-242	-120.0	-225	-111.6	-56.2	-27.88	0.977

+All species taken as ideal gases. <sup>†</sup>Environment taken as: 25°C, 1 bar, 363 ppm CO<sub>2</sub>, 2% H<sub>2</sub>O, 20.48% O<sub>2</sub>, balance N<sub>2</sub>.

\*Reaction with stoichiometric air at 25°C, 1 bar. All products present as ideal gases, including water.

The Conversion Efficiency potential (maximum first-law efficiency based on LHV) of most hydrocarbon fuels is ~106%.

# Progress to Date

- Investigated use of simultaneous work extraction during combustion to **reduce irreversibility** in engines (motivated by fuel cell).
  - Proved that for adiabatic systems, complete combustion before expansion is optimal. (2004 GCEP Report)
  - Demonstrated that efficiency increase of ~10% can be achieved by reduced heat loss through late-phased combustion. (2004 GCEP Report)
  - For non-adiabatic systems, showed that optimization of the extraction profile can improve efficiency ~10%. (K.Y. Teh, Poster Session)
- Investigated the conditions necessary for **reversible engines**.
  - Used reverse engineering of the PEM fuel cell as a vehicle to enhance understanding. (2004 GCEP Report)
  - Showed that pressure can restrain reaction. A reversible expansion engine with  $\Delta_r G \sim 0.2$  eV is possible. (S.L. Miller, Poster Session)
- Significant progress in developing a **systematic understanding** of engine efficiency regardless of engine type. (The subject of this talk)

# Improving Engine Efficiency by Exergy Management

- Exergy:

$$X = PE + KE + X_{thermal} + X_{chemical}$$

- Balance:

$$\underbrace{dX_{resource}}_{\substack{\text{Accumulation or} \\ \text{Depletion of the} \\ \text{Exergy in Resource}}} = \underbrace{\delta X_{in} - \delta X_{out}}_{\substack{\text{Transfers of Exergy} \\ \text{into or out of Resource} \\ \text{as work, heat, or matter}}} - \underbrace{\delta X_{destroyed}}_{\substack{\text{Destruction of Exergy} \\ \delta X_{destroyed} = T_o \delta S_{gen} \geq 0 \\ \text{(Gouy-Stodola Theorem)}}$$

- Incomplete Extraction
- Compounding
- Preparing Resource
- Losses from System
- Device Irreversibility
- Unrestrained Reaction

- Transfers:

$$W_{env. boundary} \rightarrow \delta X = (P - P_o) dV$$

$$\text{Other } W_{rev} \rightarrow \delta X = \delta W$$

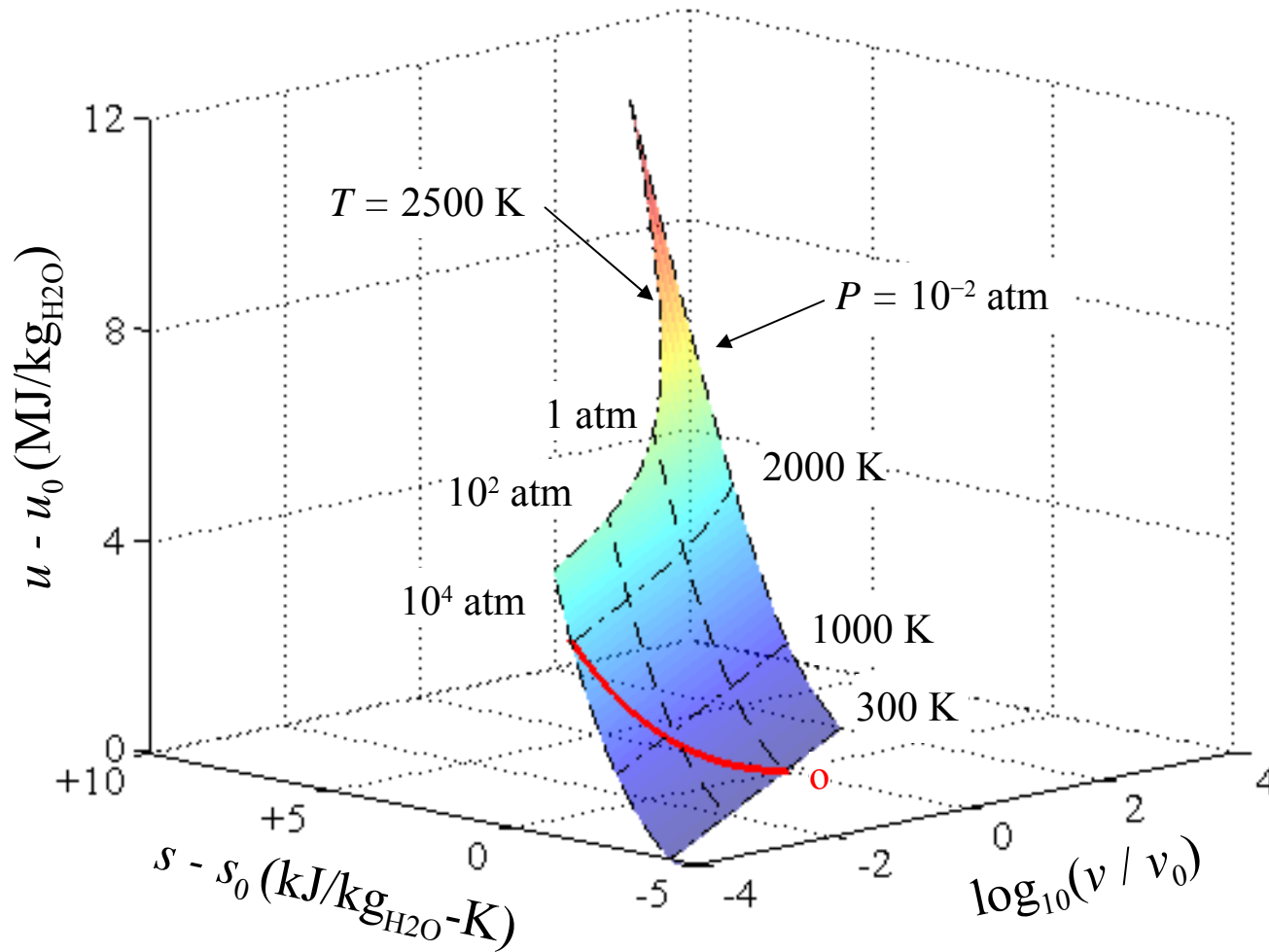
$$\text{Heat} \rightarrow \delta X = \delta Q (1 - T_o/T)$$

$$\text{Matter} \rightarrow \delta X = [\bar{x} + (P - P_o)\bar{v}] \delta N$$

# Extraction

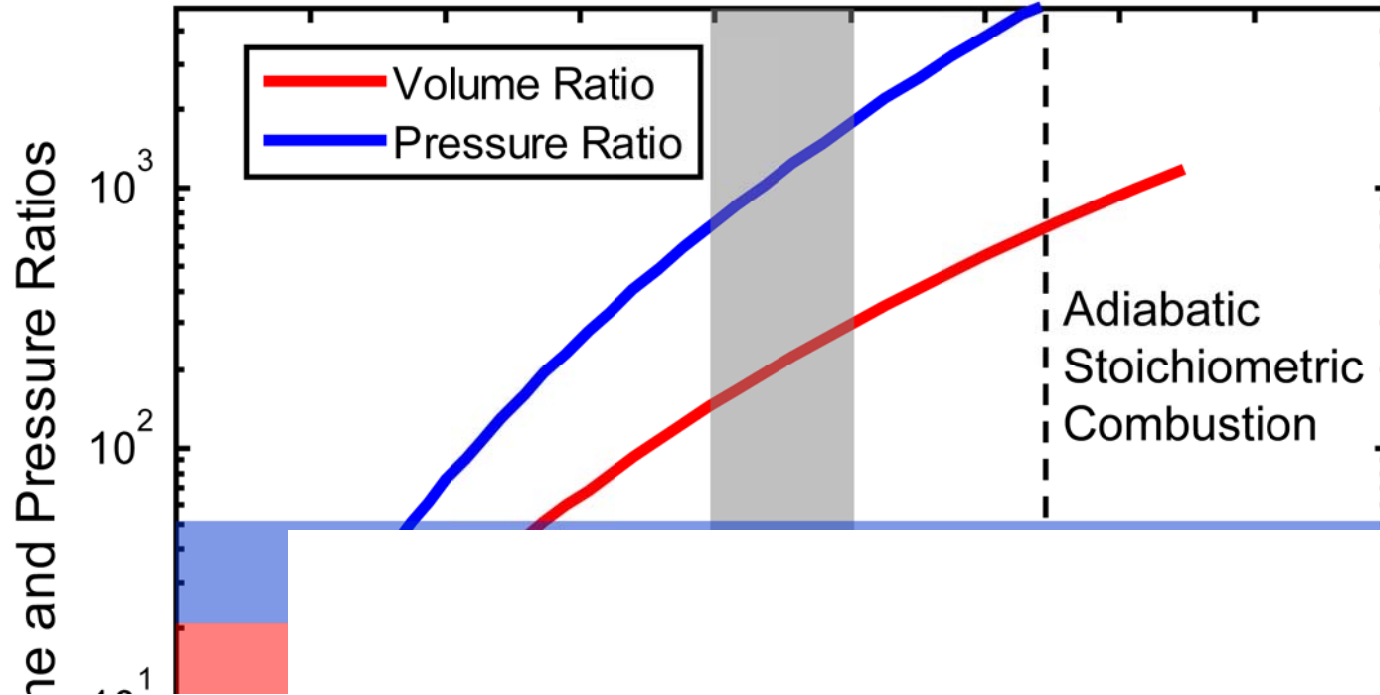
- Types of work-extraction machine
  - Impulse turbine: water, wind (kinetic energy)
  - Electric motor: electrons (electrical energy)
  - Batch expander: gas, vapor,  $PdV$  (thermal energy)
  - Flowing expander: gas, vapor,  $VdP$  (thermal energy)
- The connection to the environment holds the exit pressure or temperature (but not both) near that of the environment.
  - Expanders that use reaction products as a working fluid discharge entropy to the environment through matter.
  - Expanders that use a closed cycle with a tailored working fluid discharge entropy through heat.
- None of these work-producing machines intentionally use chemical reaction. (Reaction is completed before extraction.)

# Reversible Expansion\*

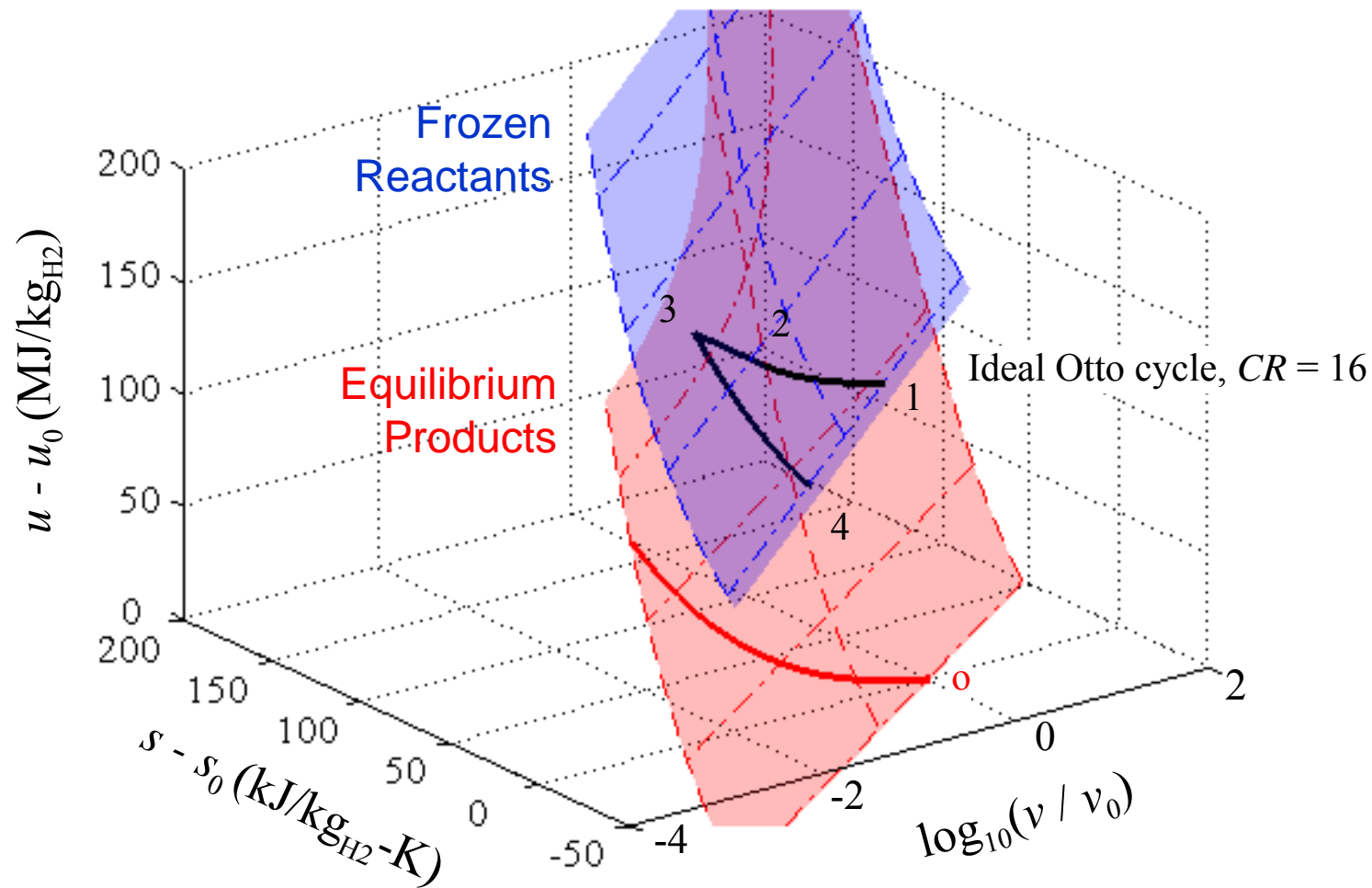


\*Water but with dissociation included  
(e.g., OH appears at high temperatures)

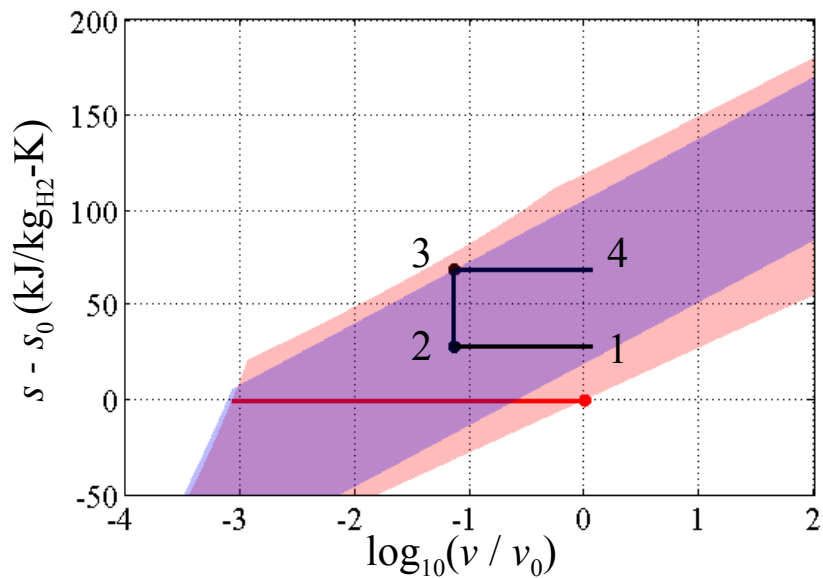
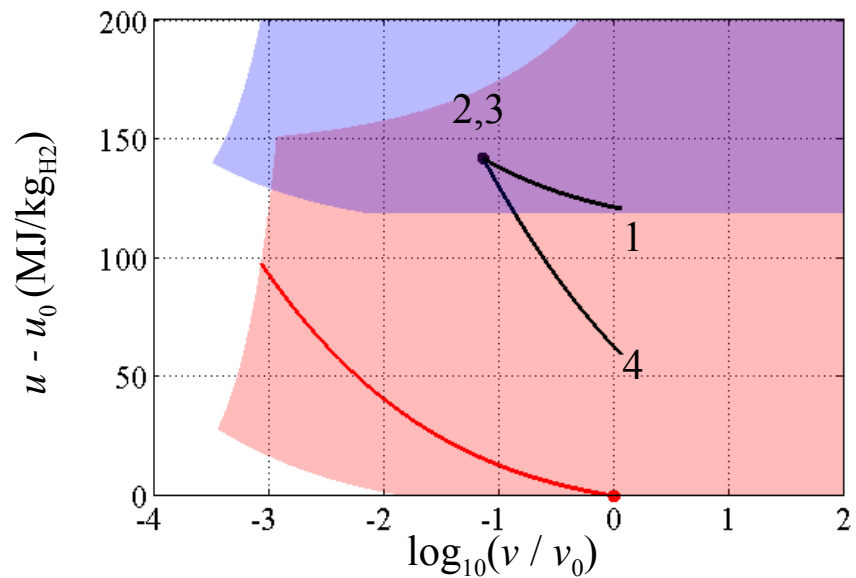
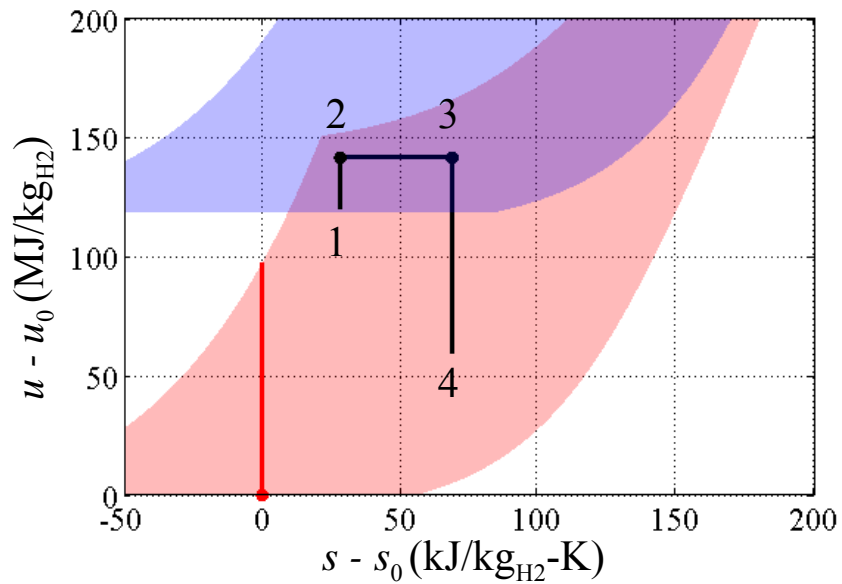
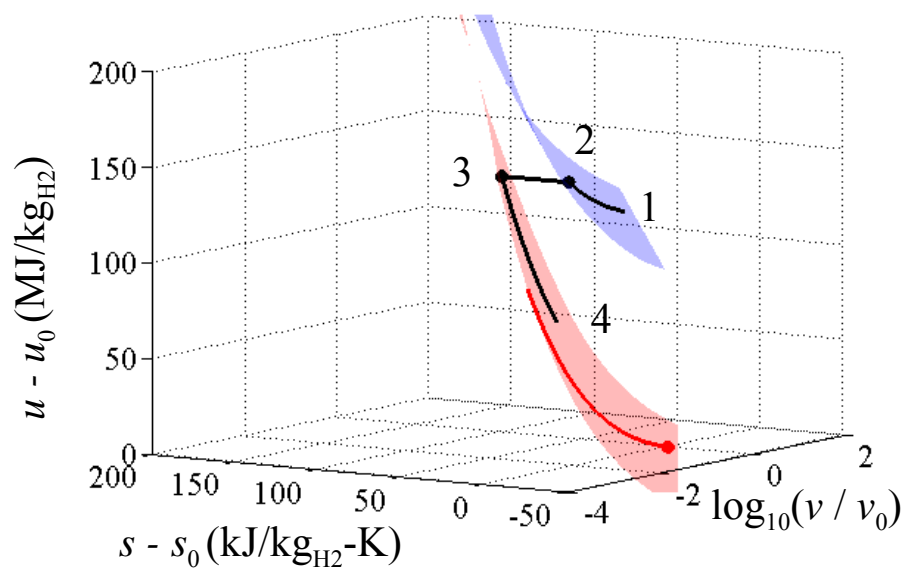
# Product Gas Expansion\*



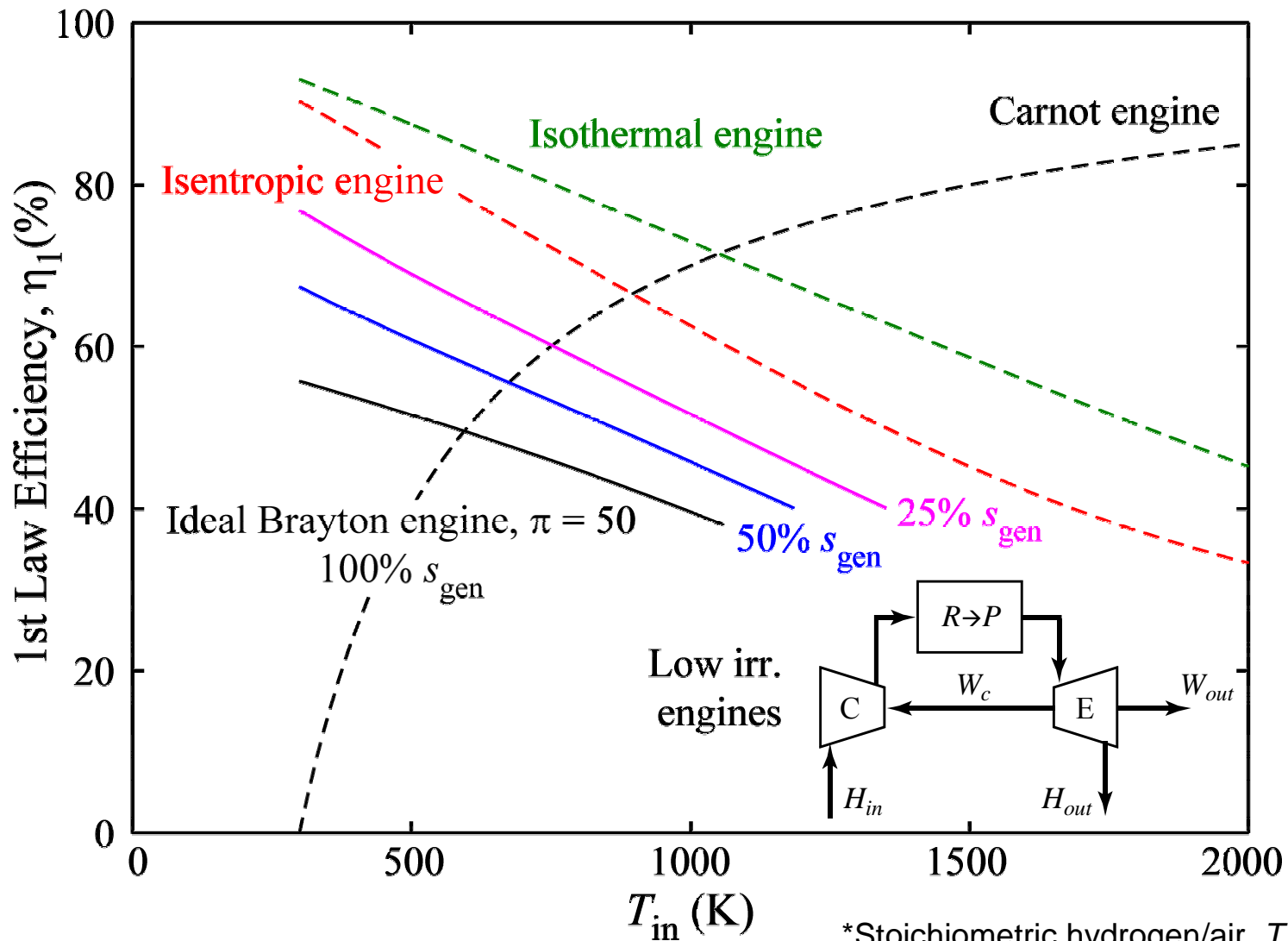
# Combustion Irreversibility\*



\*Stoichiometric hydrogen/air mixture  
Frozen reactants, equilibrium products



# Effect of Reducing Irreversibility\*



# Reversible Reaction

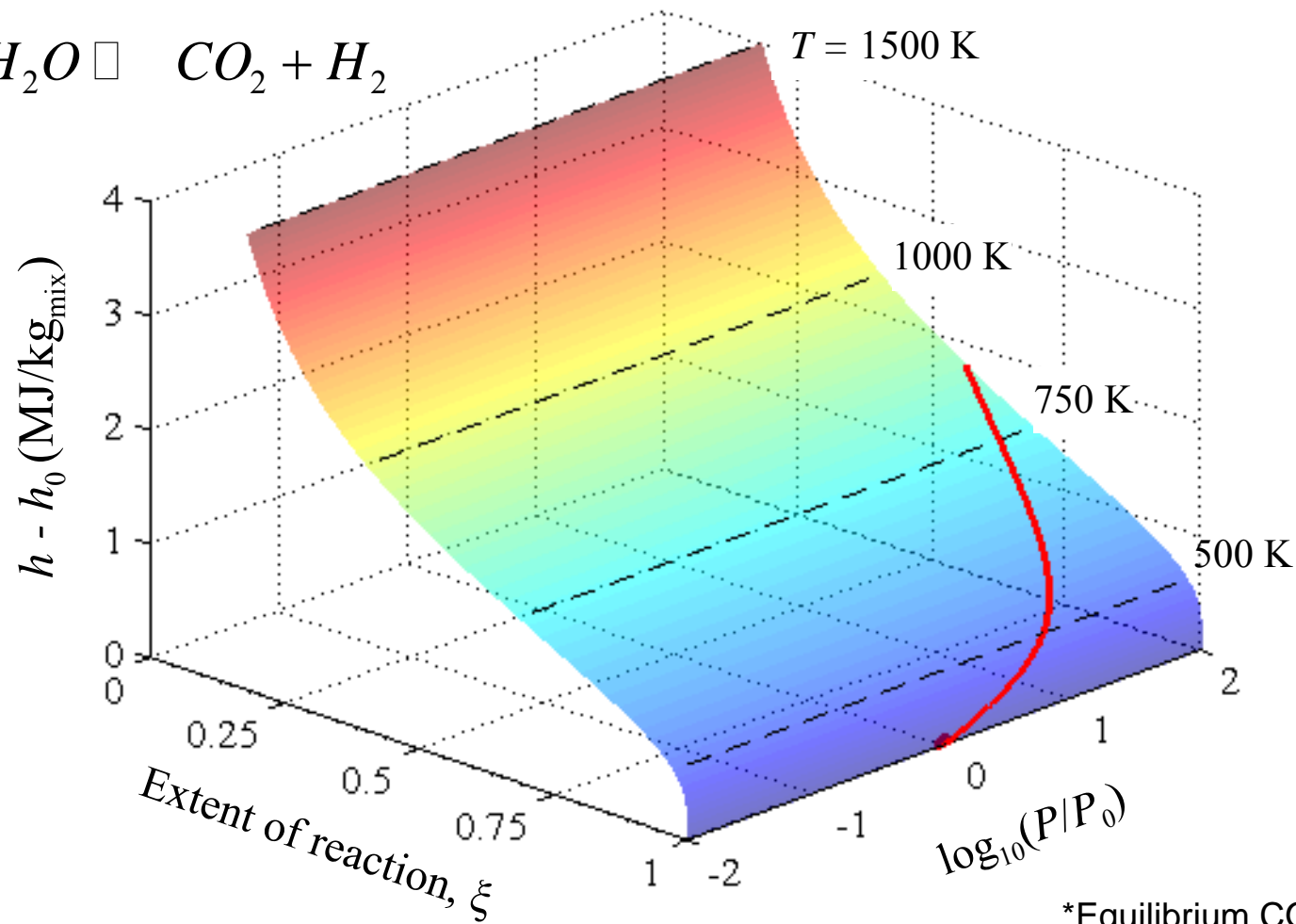
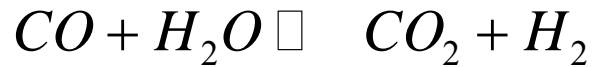
- **Entropy generation** is not permitted, but entropy transfer (and therefore change) is possible.
- **Internal restraints** are not permitted
  - Chemical pathways must be kinetically open or closed, not in between. (Frozen or equilibrium, not rate limited)
  - Requires catalytically selective pixie dust
- **External restraints** are absolutely required
  - Work provides an entropy-free transfer of energy.
  - Heat provides an entropic form of energy transfer.
  - Matter provides a mixed mode of energy transfer.
  - Requires adiabatic compressor/expander (work), thermal pixie conductors (heat), species-selective pixie conductors (matter)

# Pixie Parts

- Pixie parts are devices that permit reversible reaction within, or interaction with, the resource.
  - The **time scale of reaction** must be either very fast (kinetically open) or very slow (kinetically closed) with respect to the interactions that restrain the process.
  - The **length scale of both reaction and interaction** must be small with respect to the scale of thermal diffusion.
- Since the time scale for pressure relaxation is much faster than thermal relaxation, **boundary work** can be used as form of restraint (no pixies required!).
- Pixie parts are available from the same vendors that supply *unobtainium* (the metal that can withstand any temperature and stress) and *adiabatic spray paint*.

# Syngas to Hydrogen\*

- Water-Gas Shift Reaction:



\*Equilibrium CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O  
Atom Ratios C:H:O = 1:10:3

# Fuel to Syngas\*

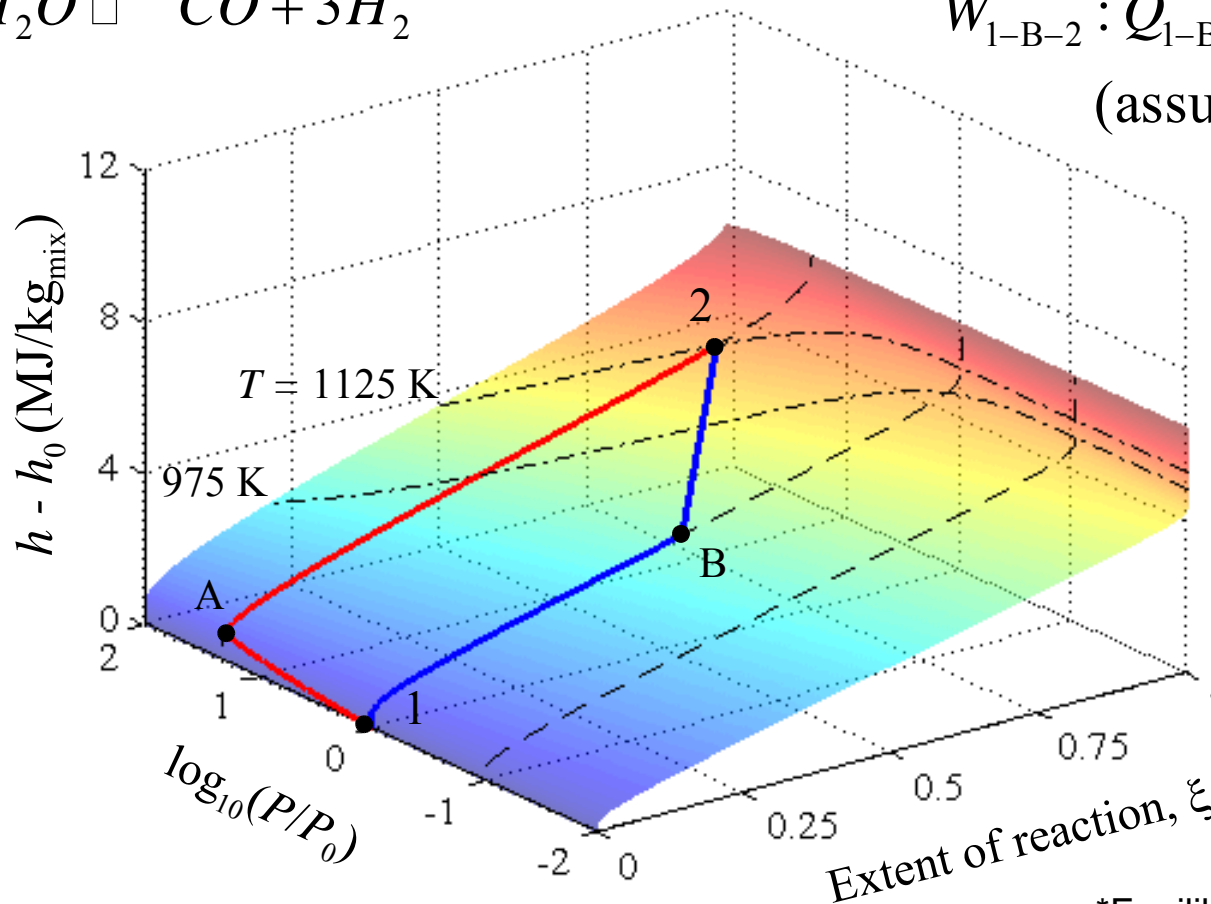
- Steam Methane Reforming Reaction:



$$W_{1-A-2} : Q_{1-A-2} \rightarrow 0.15 : 0.85$$

$$W_{1-B-2} : Q_{1-B-2} \rightarrow 0.40 : 0.60$$

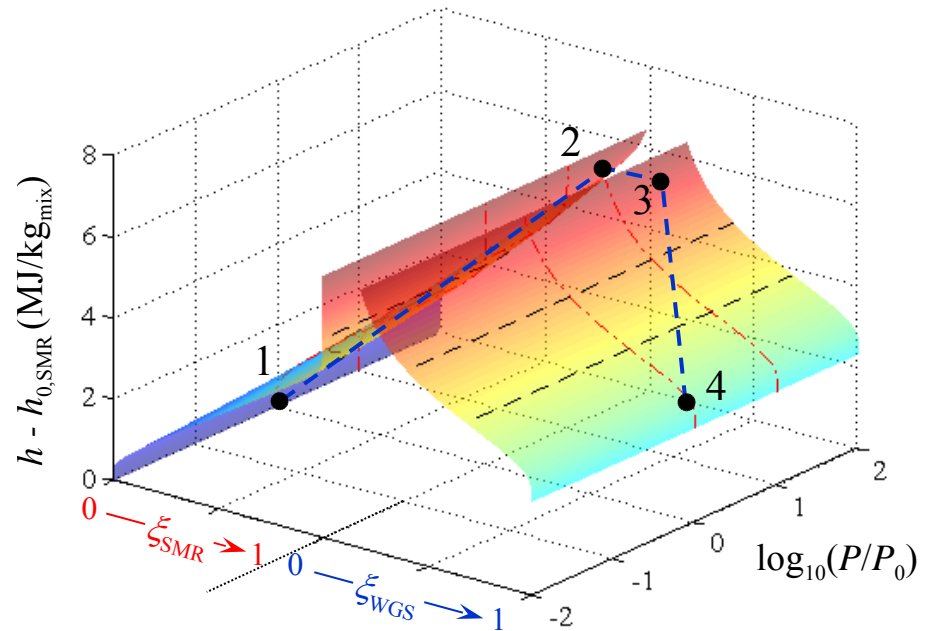
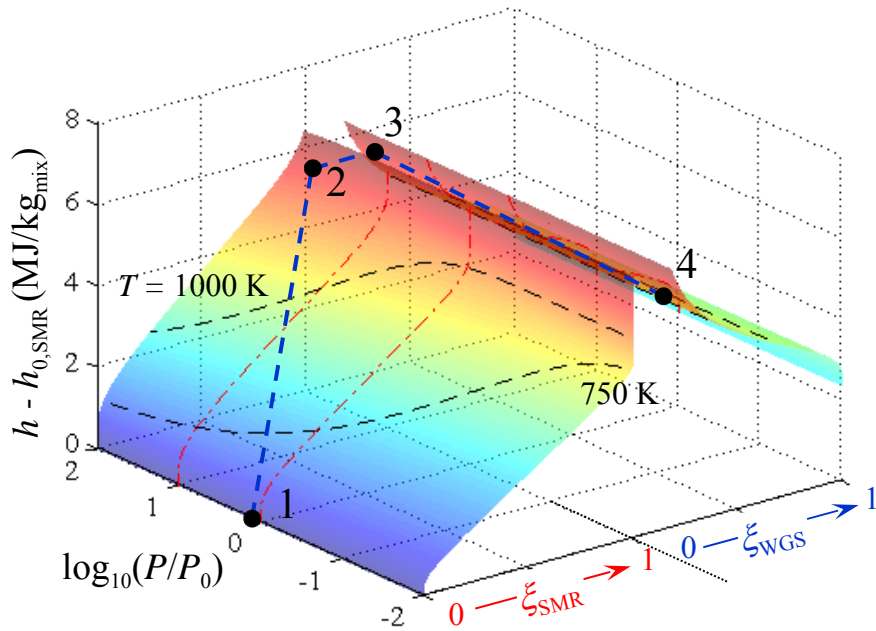
(assuming no WGS)



\*Equilibrium CO, CH<sub>4</sub>, H<sub>2</sub>, H<sub>2</sub>O  
Atom Ratios C:H:O = 1:10:3

# Multiple Reactors\*

- Perfectly selective reactors in series, SMR then WGS:



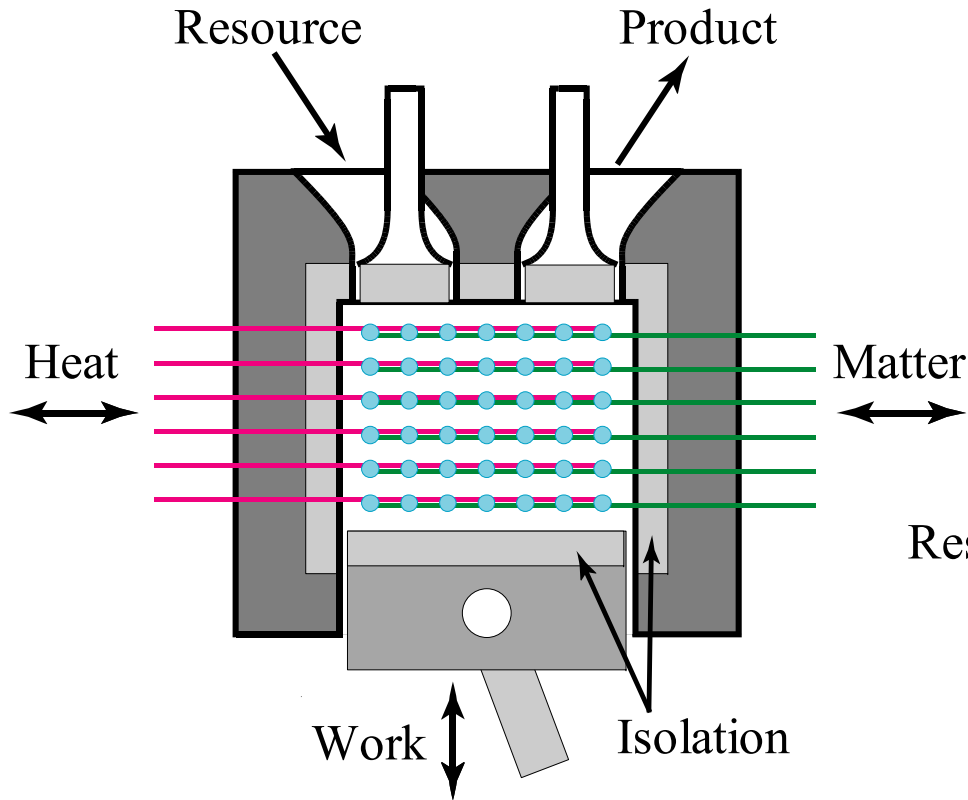
- The surface jump ( $CO_2$  generation) is avoided by allowing both SMR and WGS to proceed in the first reactor.

\*Equilibrium  $CH_4$  or  $CO_2$ ,  $CO$ ,  $H_2$ ,  $H_2O$   
Atom Ratios C:H:O = 1:10:3

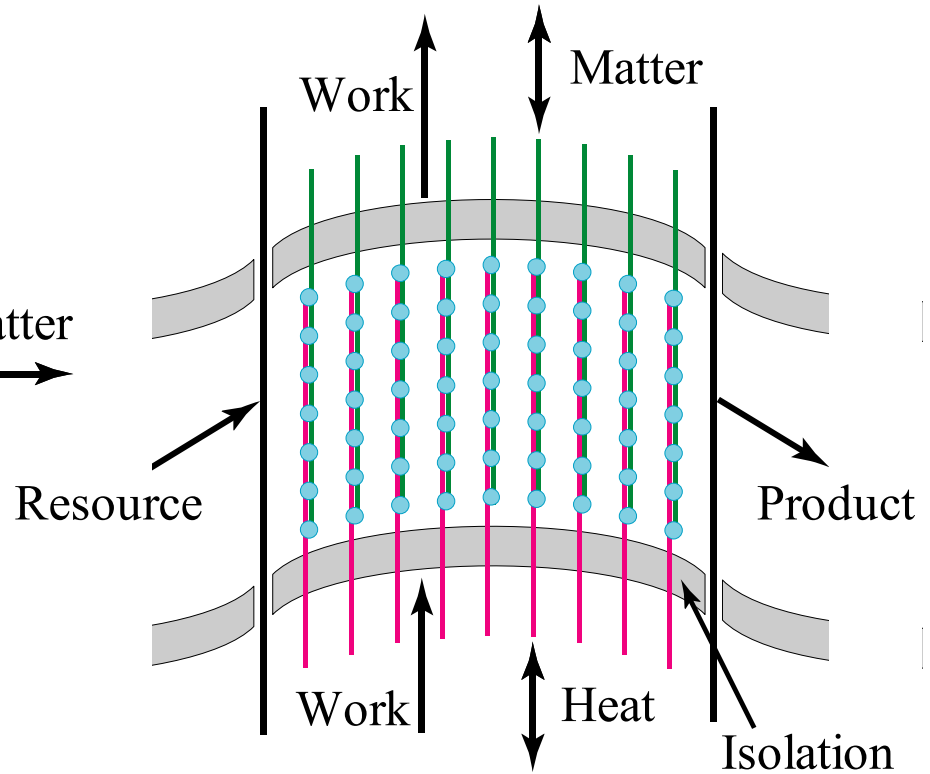
# Getting to Products

- Essentially all the carbon can be taken to product (carbon dioxide) by WGS.
- All of the chemical exergy has been transferred to the hydrogen.
- Oxidation of the hydrogen to water is still required.
  - If accomplished irreversibly, must position resource to minimize exergy destruction.
  - Still not clear whether we can find a reversible path other than through electrochemistry. (Pressure ~ 0.2 eV)
- An opportunity for carbon separation exists here if suitable membranes are available.  
(See ECN/TU Delft *new-project talk* on Thursday)

# Reversible Reactors

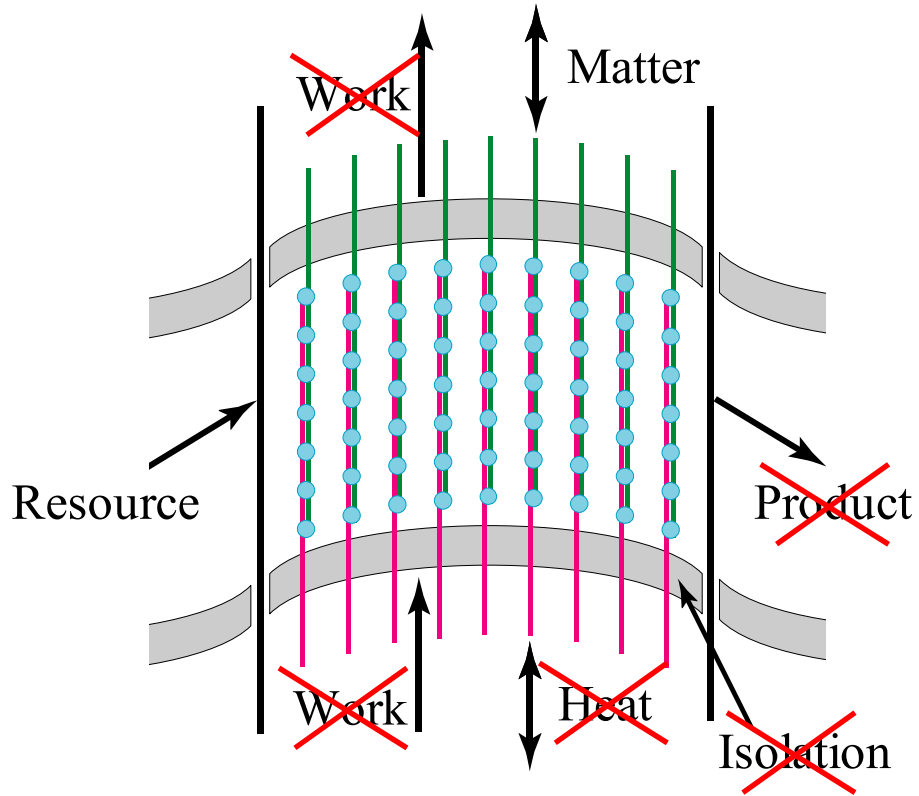


- Batch (Piston/Cylinder)

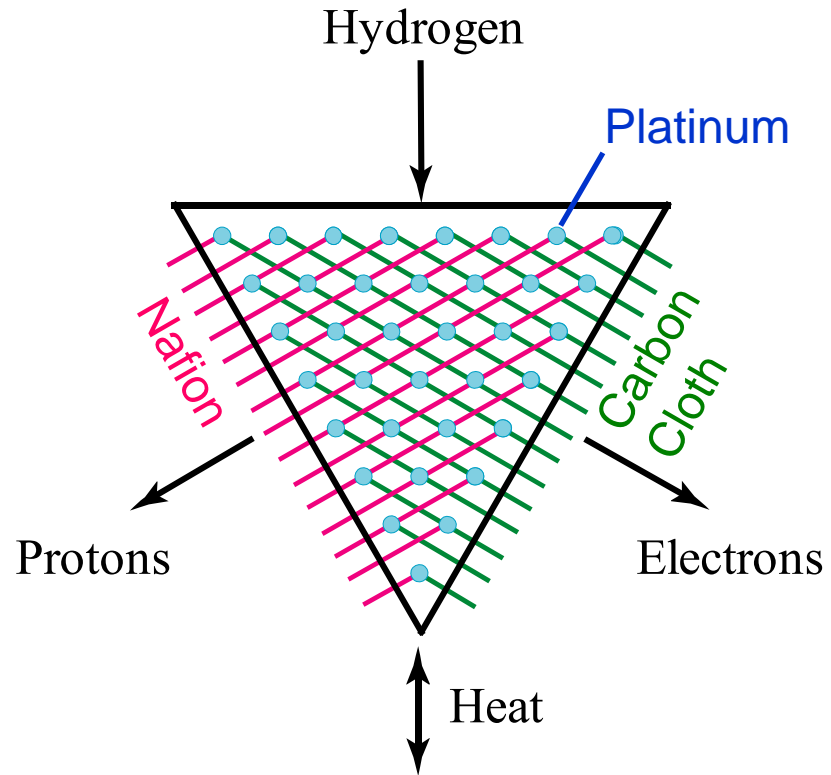


- Steady Flow (Turbine)

# A Simplified Flow Reactor

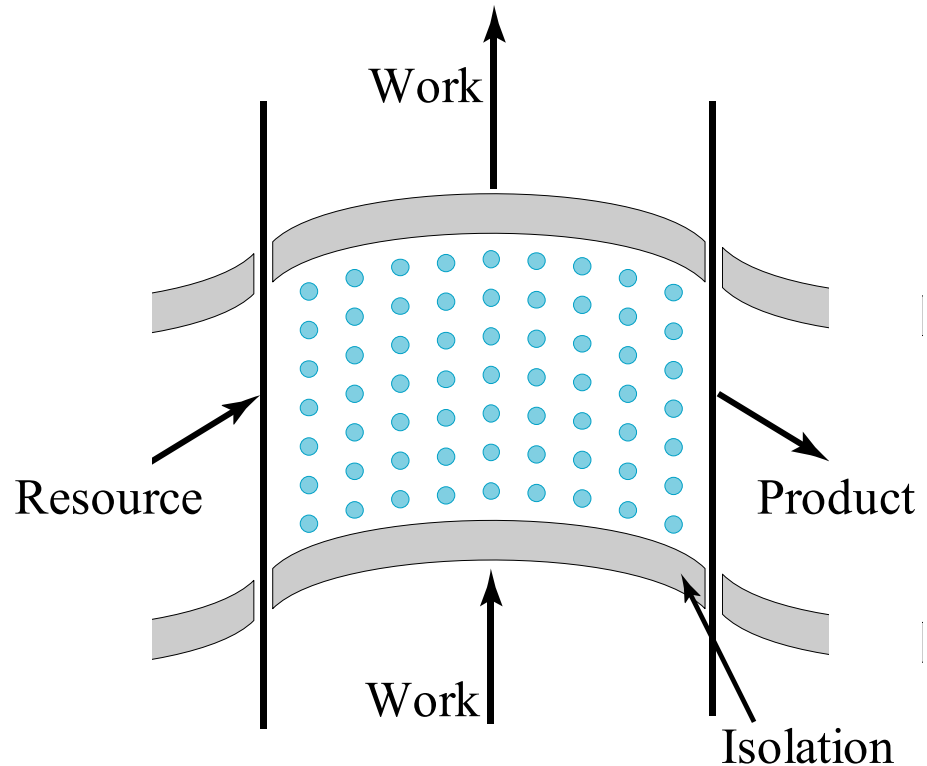
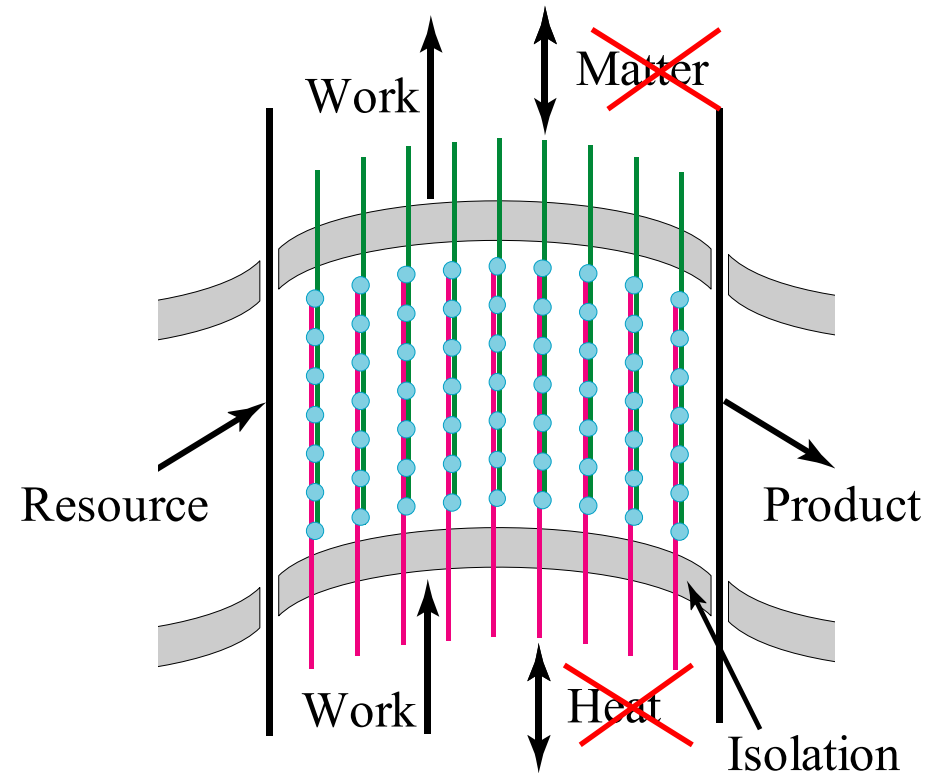


- Steady Flow Device



- PEM Fuel Cell Anode

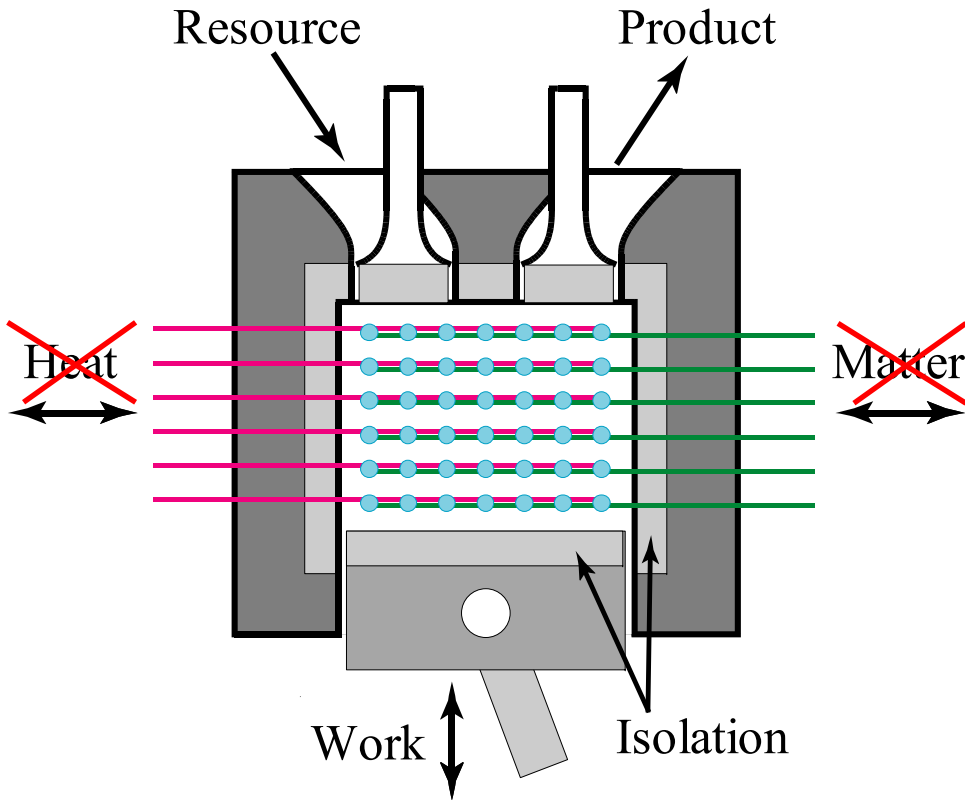
# Another Simplification



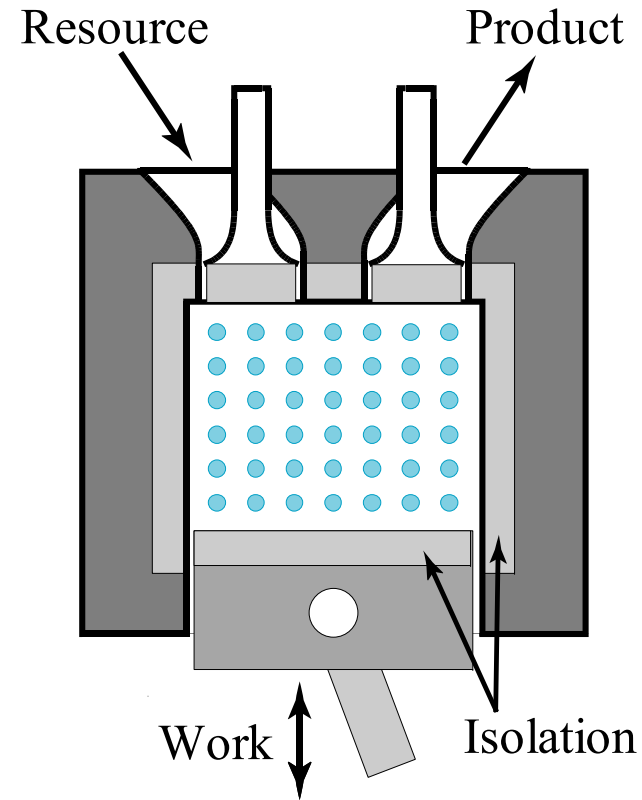
- Steady Flow Device

- Adiabatic Compression-Expansion Flow Reactor

# A Simplified Batch Reactor

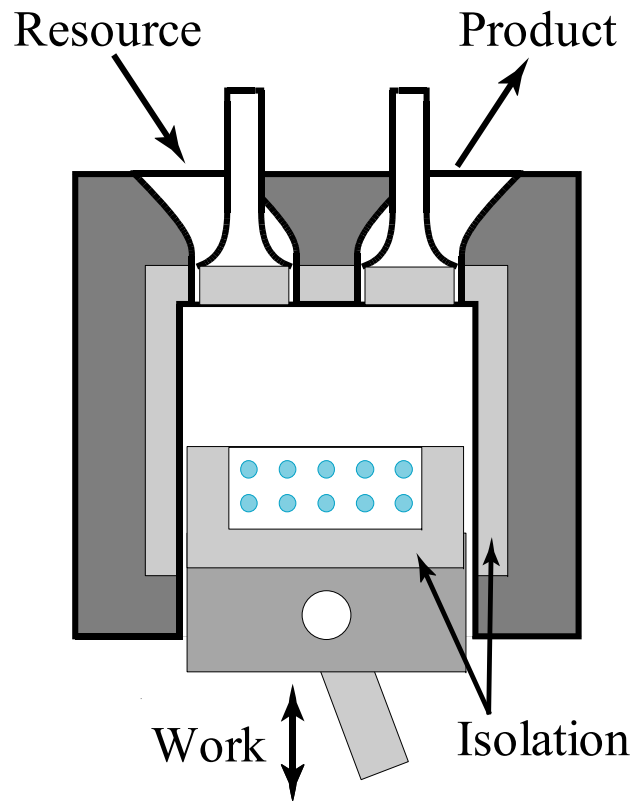


- Batch (Piston/Cylinder)



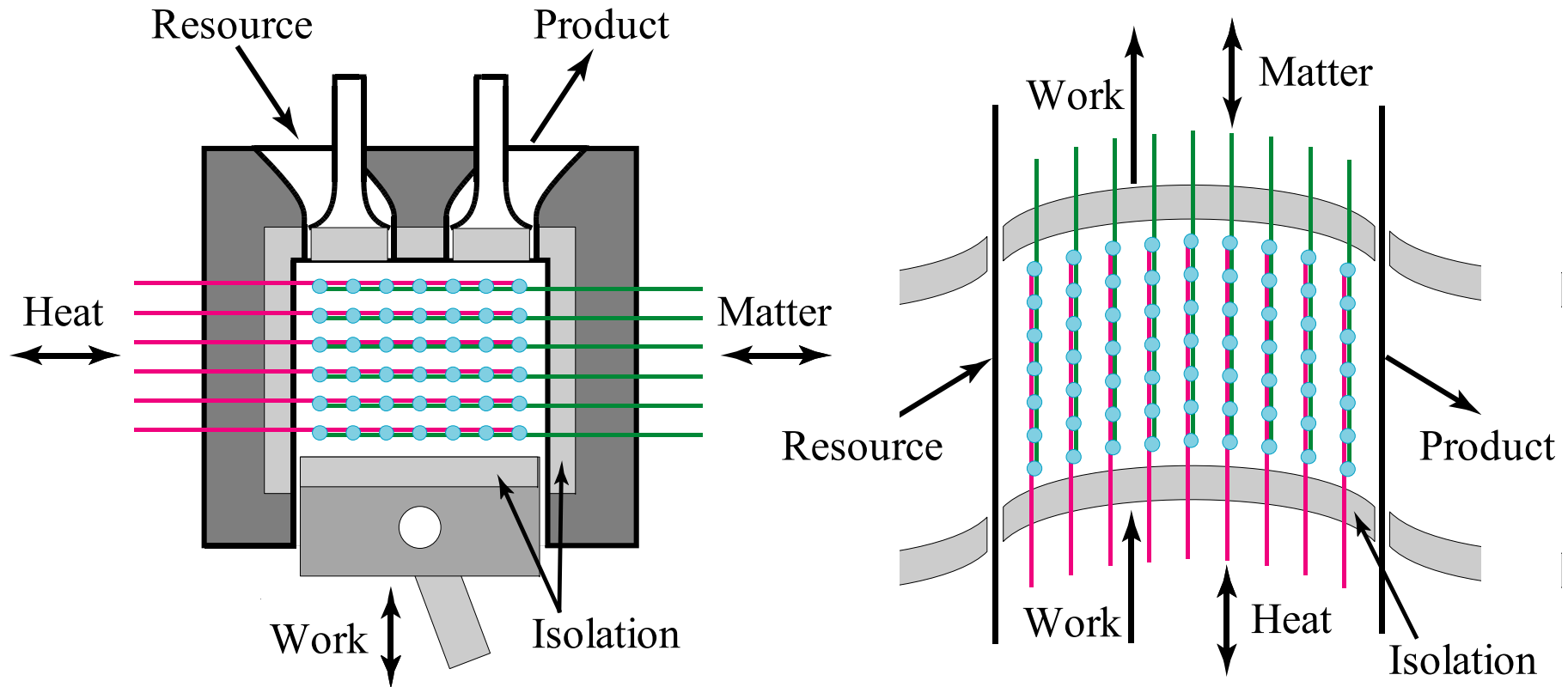
- Adiabatic, Catalytic, Regenerative Engine

# Further Simplification...



- A Practical Engine?
- Exergy loss to **coolant** is eliminated (not recoverable).
- Peak combustion **temperature** is reduced to material limits (dilute, HCCI-like).
- Catalytic material lowers **initiation** temperature.
- Thermal mass lowers **peak** temperature (regeneration).
- **Exergy is retained** in the working fluid for downstream extraction (compounding).
- Turbocharging can be used to provide **power density**.

# Reversible Reactors

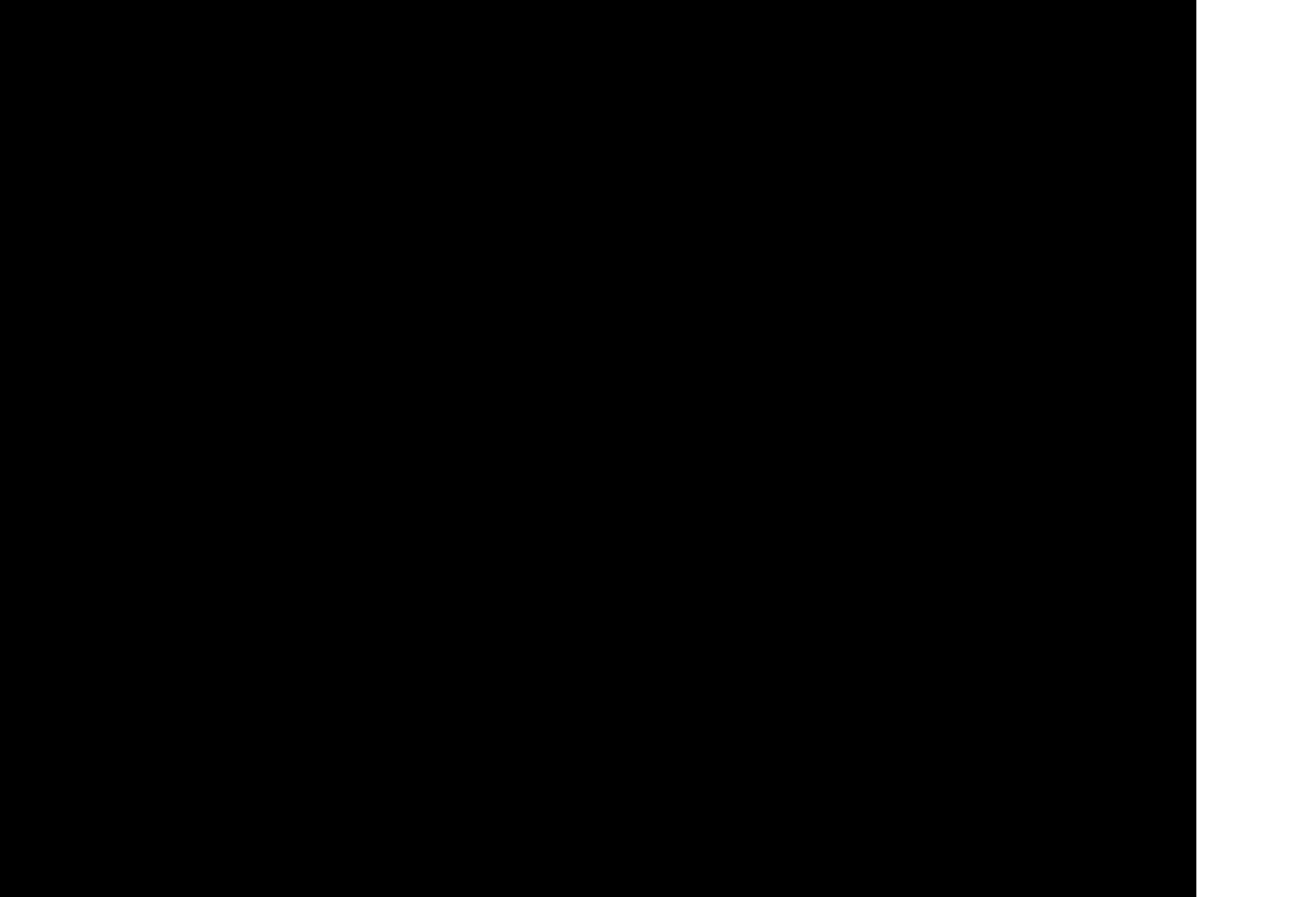


Are you sure it is impossible?

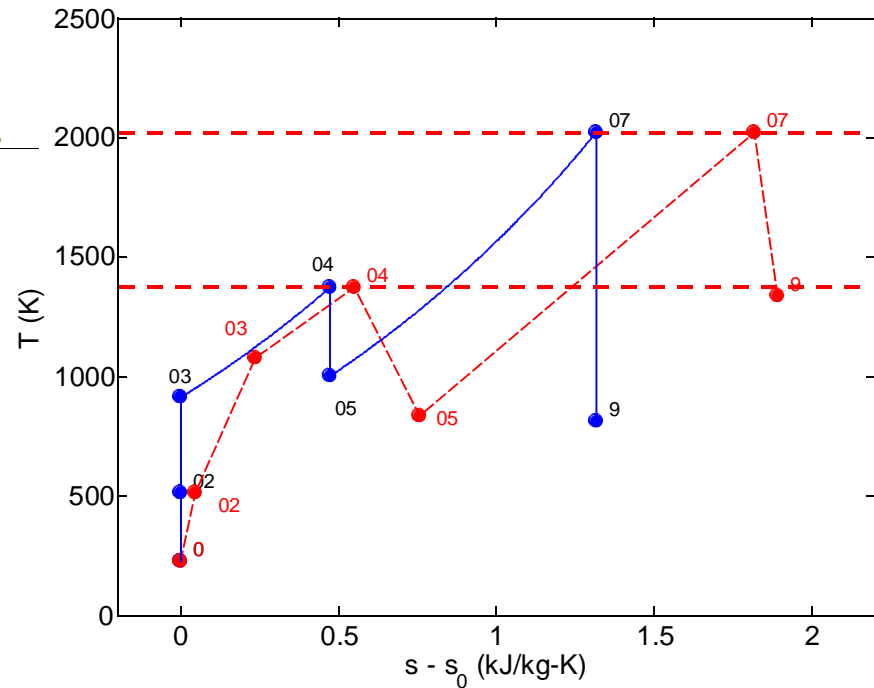
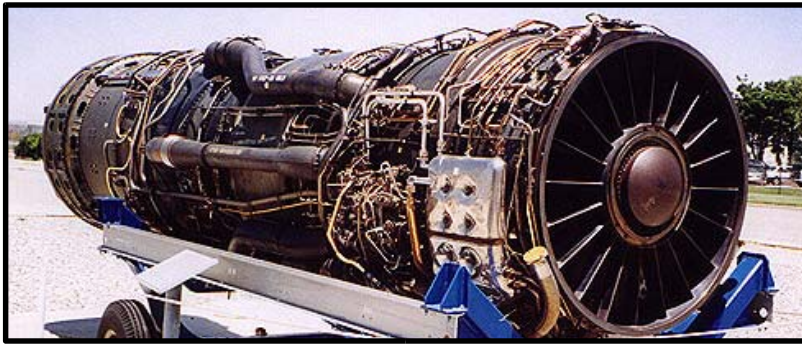
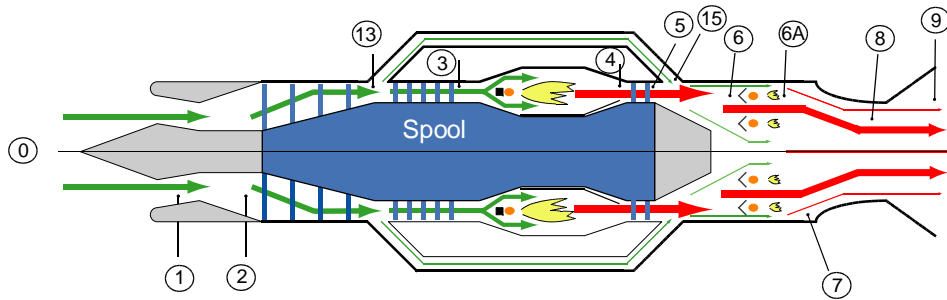
The payoff for success is a doubling of efficiency!

# Conclusions

- Efficiency of simple-cycle engines can be more than doubled—current exergy efficiencies are less than 50%.
- The key to systematically improving engine efficiency (both simple and compound) is exergy management.
- Extractor limitations and the mis-match of combustion to product-gas expansion severely limits simple-cycle efficiency.
- Exergy loss due to heat transfer in piston engines must be reduced or eliminated. This enables compounding.
- Exergy destruction due to combustion must be reduced or eliminated.
  - Reduced irreversibility can be achieved by positioning of reactants.
  - Reversible reaction is possible. Making it practical is the challenge.
- Use of hybrid or compound architectures significantly alters what is possible by eliminating design tradeoffs (e.g., power vs. efficiency). Re-consideration of topping and bottoming methods is warranted.



# Architecture vs. Device-Level Design



- System Architecture: ideal devices, real limits
- Device-Level Design: real devices, same limits

Exergy loss occurs due to both system architecture and device implementation. In many cases, it is ultimately the architecture that limits the efficiency of an engine, not the devices.

# Three Components of Architecture

All chemical engines use one or more stages of three basic processes:

- **Preparation**
  - Combining and positioning resources to enable reaction and extraction
- **Reaction**
  - Activation and transformation of the resource to a more extractable chemical form
- **Extraction**
  - Conversion of resource exergy to work

# Example: S.I. Engine

- Resources
  - Gasoline
  - Matter and heat exchange with the environment
- Preparation
  - Mixture formation (air from environ., stoichiometry)
  - Compression (work addition to optimize extraction)
- Reaction
  - Spark ignition (thermal activation)
  - Combustion (unrestrained reaction to products)
- Extraction
  - Boundary work ( $PdV$  batch expansion)
  - Products discharge to environment

# Example: PEM Fuel Cell

- Resources
  - Hydrogen
  - Heat and matter exchange with the environment
- Preparation
  - Humidification, air from environment, compressor work
- Reaction: Upstream/Anode
  - Platinum catalyst (electrical activation)
  - Hydrogen to protons and electrons (electron source)
- Reaction: Downstream/Cathode
  - Platinum catalyst (electrical activation)
  - Protons, electrons, and oxygen to water (electron sink)
  - Products discharged to environment
- Extraction
  - Done by electrons in a motor (a fuel cell is not an engine)
  - Motor requires a potential difference (hence two reactions)

# Example: Supercritical Rankine

- Resources
  - natural gas
  - matter and heat exchange with the environment
- Preparation
  - Air and fuel compression (pumping)
- Reaction
  - Flame holding (thermal activation)
  - Combustion (unrestrained reaction to products)
- Preparation
  - Water purification and pressurization
- Heat transfer: Upstream/Boiler
  - Exergy transferred as heat to water as extraction fluid
  - Combustion products discharged to environment
- Extraction
  - Boundary work ( $VdP$  flowing expansion)
  - No matter discharge to environment
- Heat transfer: Downstream/Condenser
  - Heat is used to reject entropy, not matter.

# Observations

- It is not engine design that sets the work that can ultimately be obtained from a resource (fuel), it is the resource itself and the surroundings in which it is utilized.
- First-law efficiencies approaching or exceeding 100% are possible and must be our design aspiration.
- The problem of engine design is best viewed as one of exergy management rather than device development.
- The objective of our work is to develop a **systematic approach** to the design of high-efficiency (low exergy loss) chemical engines.

# A Systematic Approach

- Engine architecture can be organized by considering these four features (in reverse order):
  - Interaction(s) with the environment
  - Method(s) of **Extraction**
  - Method(s) of resource **Reaction**
  - Method(s) of resource **Preparation**

# Connections to the Environment

A key design choice is the way in which the engine is permitted to interact with the environment.

- It must be connected to satisfy the **second law** (entropy must be rejected from the engine).
- Entropy can only be rejected via **heat** or **matter**.
  - Engines that use reaction products as the work-extraction medium usually reject entropy via matter.
  - Engines that use a closed loop for the working fluid usually reject entropy via heat.
- The environment also provides a reservoir from which **matter can be drawn** (oxygen, water) and into which **matter can be discharged** (products).

# Expander Limitations

- **Materials** set architecture limits
  - Maximum T based on material properties without cooling is ~1500K (~1800K with injection cooling).
  - Working fluids with higher temperatures require cooling which causes exergy loss via heat transfer.
- **Technology** development sets device efficiency
  - Current flowing expanders are nearly adiabatic but have polytropic efficiencies ~XX% (exergy destruction).
  - Current batch expanders are nearly reversible but have heat losses ~30% of LHV (exergy loss with heat).
- **Match** to working fluid sets joint performance
  - Balanced combustion generates temperatures in excess of material working limitations and practical expansion ratios.
  - Unbalanced combustion (dilute) can reduce working temperatures but causes a loss of power.
- **Tradeoffs** due to limitations
  - Expanders are often selected to optimize something other than efficiency (e.g., power, cost).
  - Hybrid or compound architectures can significantly reduce tradeoffs.

# Observations

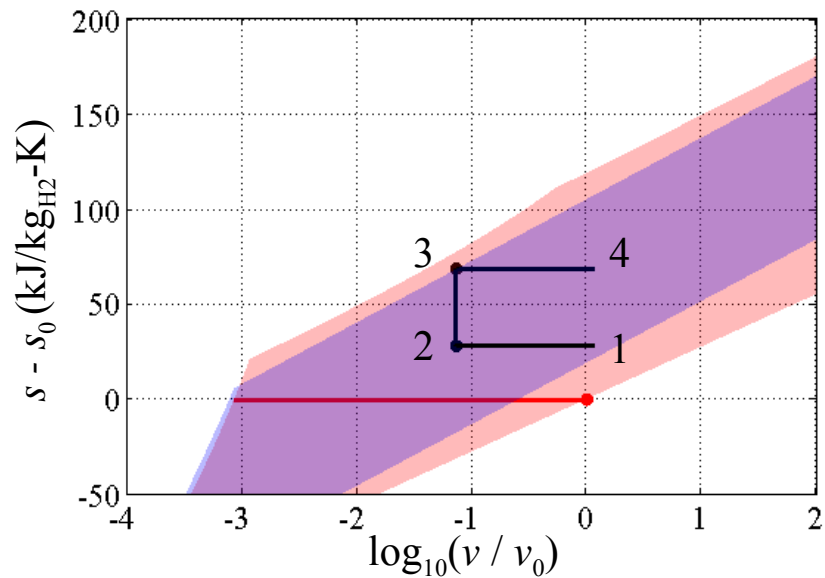
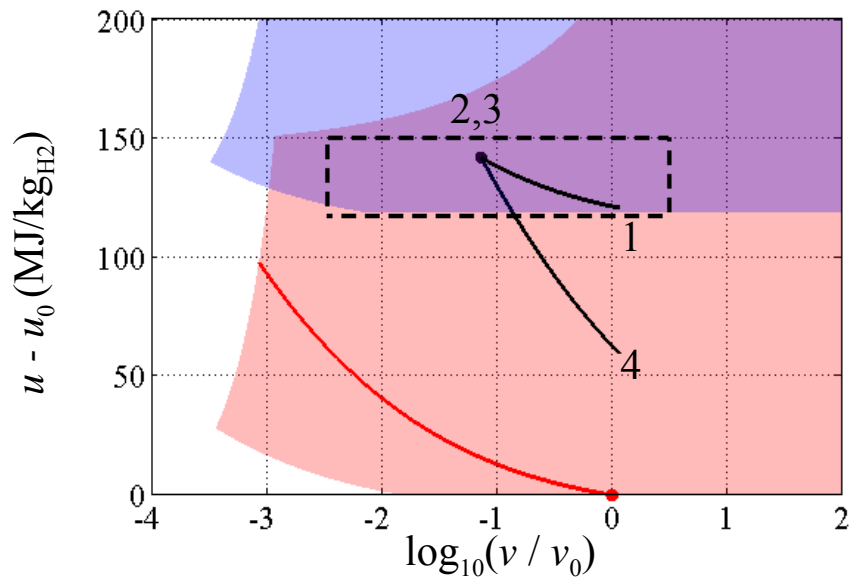
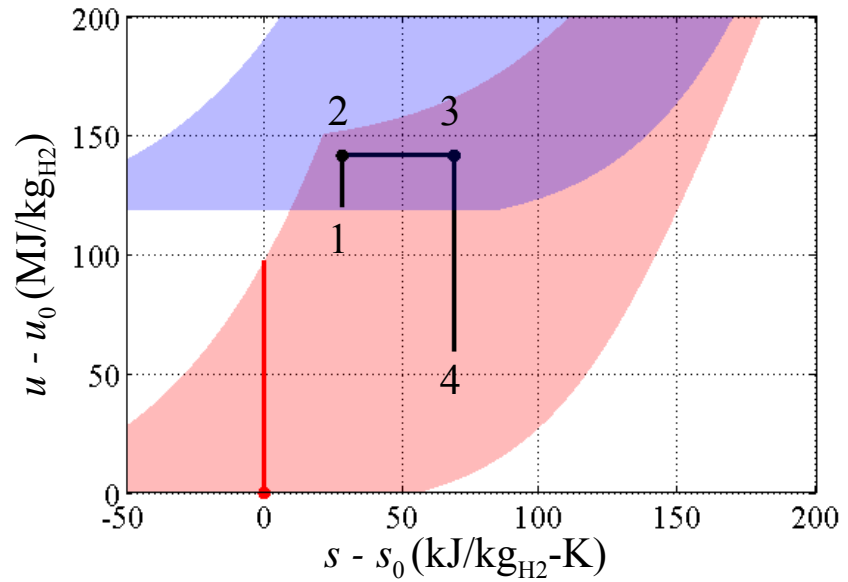
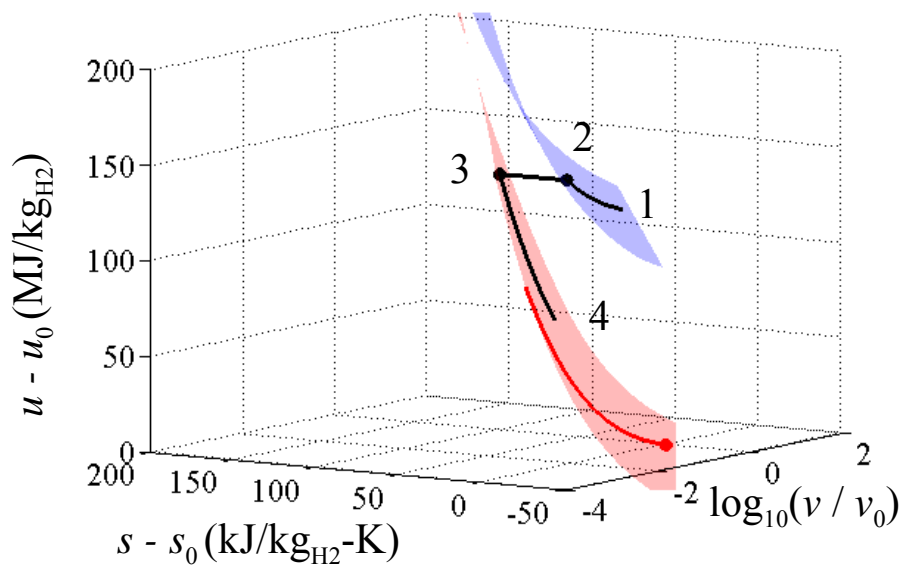
- Exergy destruction due to combustion can be reduced by **positioning the reactants** so as to minimize entropy generation subject to constraints. Key constraints are:
  - Materials limitations
  - Exergy loss with heat (non-adiabatic extraction)
  - Product gas match to the extraction device (insufficient expansion)
- **Increasing charge dilution** (not shown here) reduces irreversibility, but also results in a loss of power output.
- Irreversibility due to combustion is an **architectural loss**: It cannot be reduced by improving the design of the combustor, only by **positioning of the reactants** before combustion, or **providing restraints** on the reaction.

# Reaction

- **Irreversible**—generates entropy
  - Internally restrained (initially)
    - Combustion
    - Many forms of chemical processing (e.g., SMR, WGS)
  - “Stops” when equilibrium is achieved or kinetics are so slow as to be negligible (frozen, internal restraint).
- **Reversible**—does not generate entropy
  - Externally restrained (always)
    - Electrochemistry (electrical potential restraint)
    - Solution chemistry (chemical potential restraint)
  - Never stops, always dynamically balanced

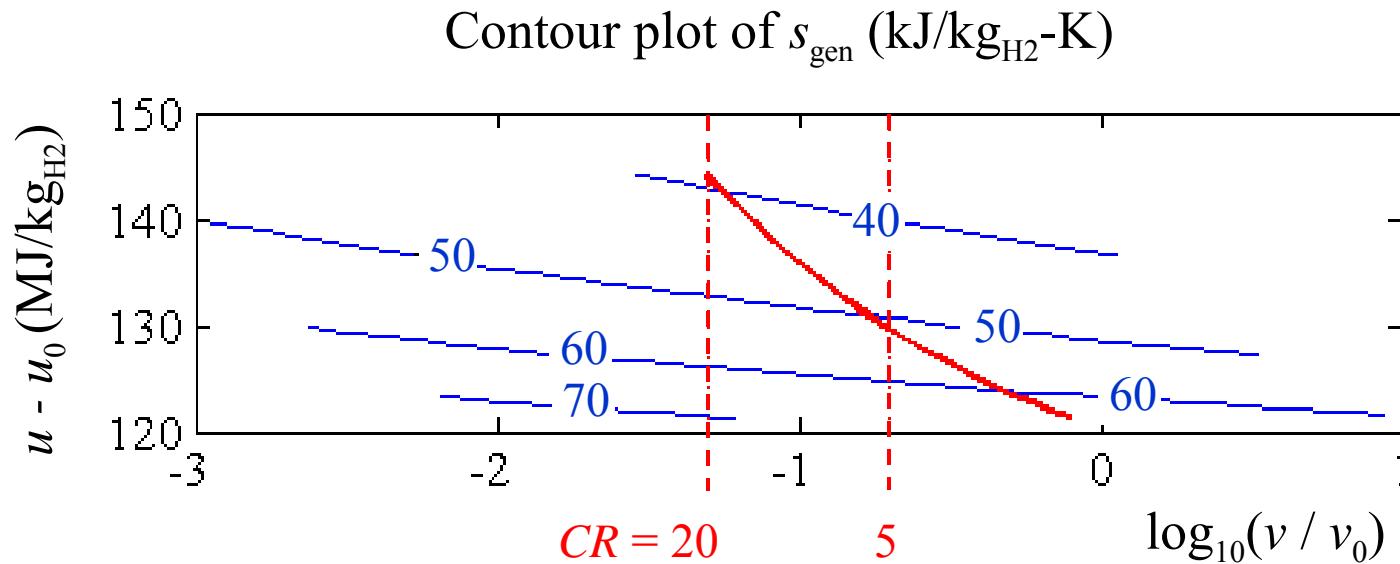
Is it possible to use less irreversible reaction methods to develop engines with improved efficiency?

Is it possible to do this by a means other than electrochemistry?



\*Stoichiometric hydrogen/air mixture

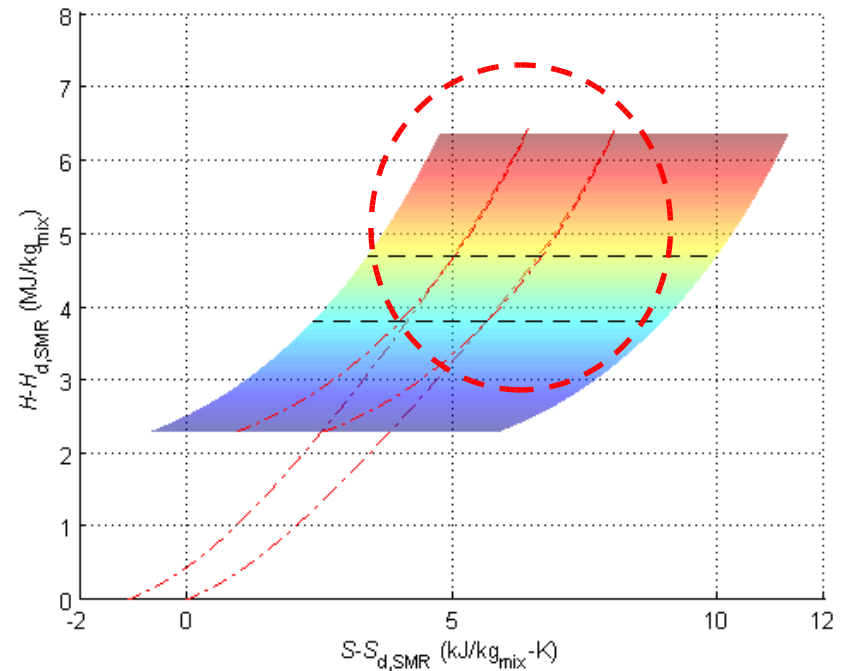
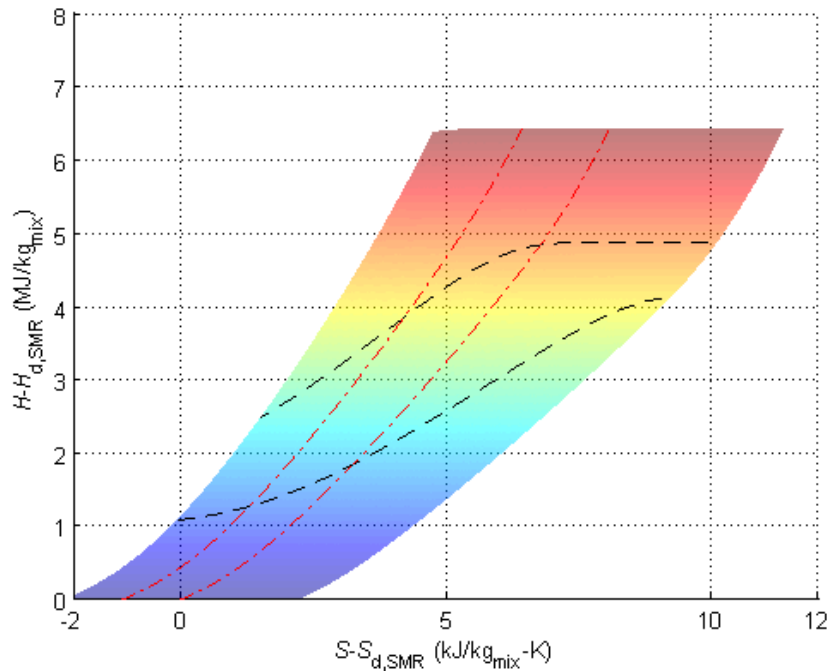
# Reducing Combustion Irreversibility



- Entropy generation due to combustion is reduced by starting with higher pre-combustion U and V (e.g., by heating).
- This is an effect of dissociation in the product gases bringing the product surface closer to the (frozen) reactant surface.
- Raising compression ratio reduces irreversibility, but not as effectively as preheating.

# Jumping Surfaces\*

- Perfectly selective reactors in series, SMR then WGS:



- The entropy generation (and therefore lost work) due to the surface jump is negligible at conditions of interest.

\*Equilibrium  $\text{CH}_4$  or  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$   
Atom Ratios C:H:O = 1:10:3

# Work and Heat Interactions

- Confine consideration of interactions to transfers of work and heat only.
- Consider a flowing system undergoing a differential change of state.

(A steady-flow reactor with unit flow rate.)

$$[E]: h + \delta w + \delta q = (h + dh)$$

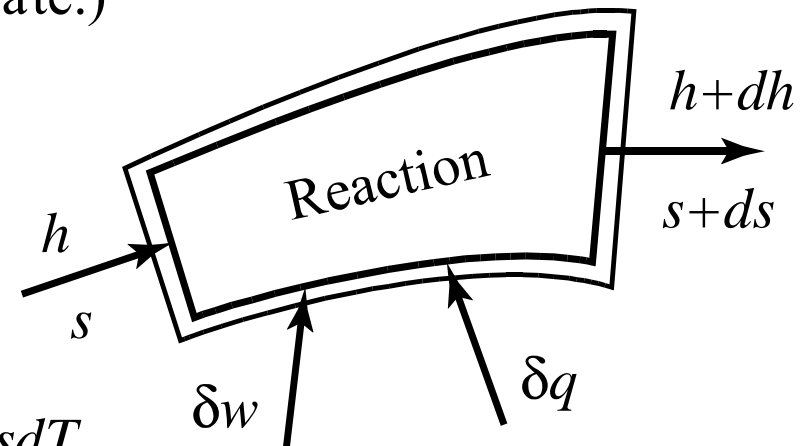
$$[S]: s + \frac{\delta q}{T} + \delta s_{gen} = (s + ds)$$

$$\Rightarrow \delta w = dh - Tds + T\delta s_{gen}$$

$$\delta w_{rev} = dh - Tds = dh - d(Ts) + sdT$$

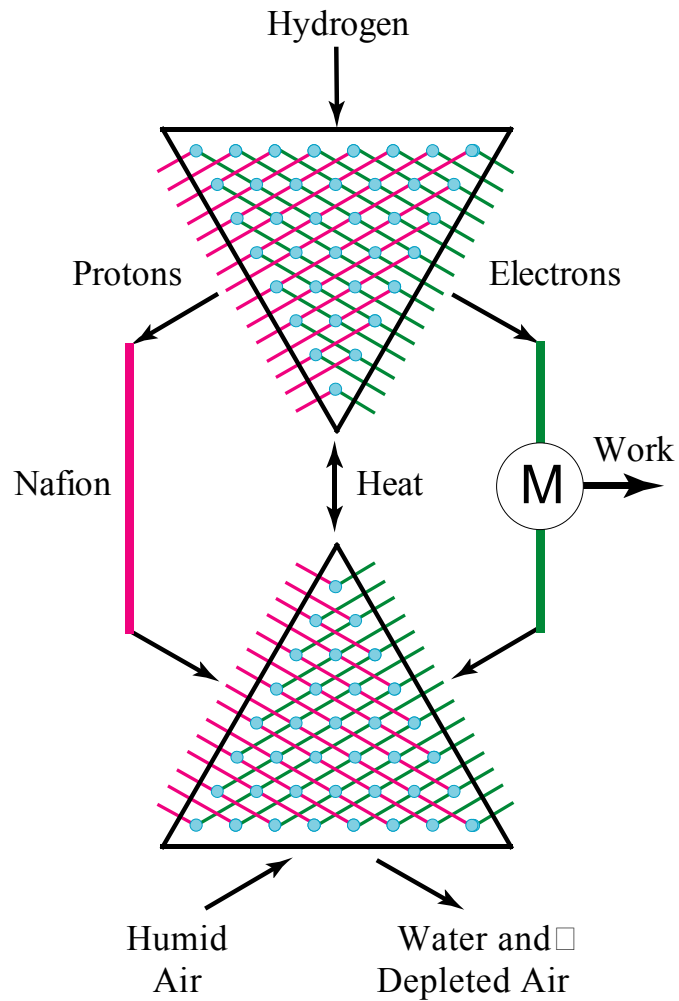
$$\Rightarrow w_{rev}_{12} = \Delta g + \int_1^2 sdT$$

$$q_{rev}_{12} = \Delta h - w_{rev}_{12}$$

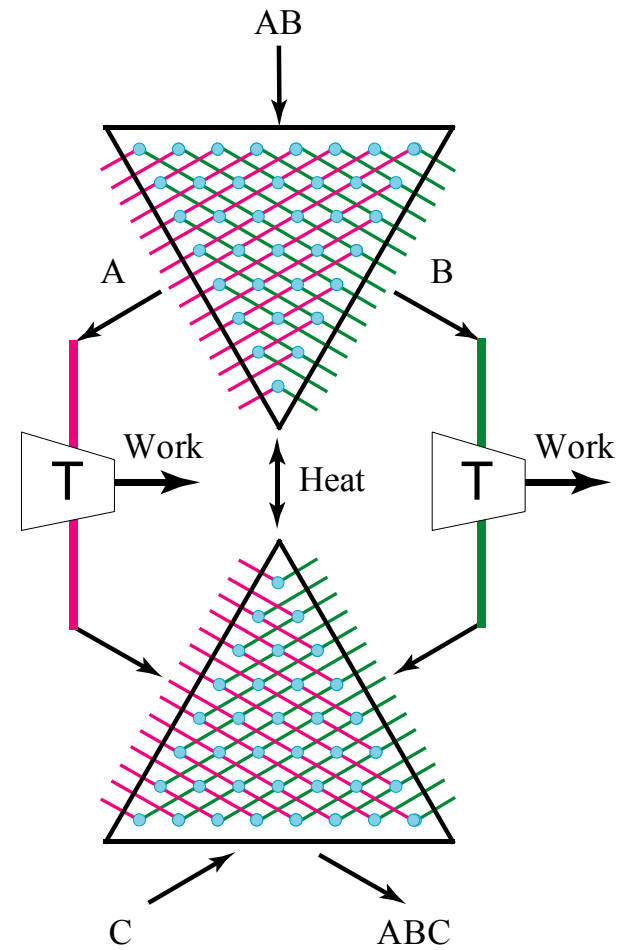


The work and heat interactions between any two states are path functions of the surface trajectory chosen between the states.

# Reversible Engines



- PEM Fuel Cell & Motor



- Rev. Expansion Engine

# Restraint via Pressure

$-\Delta_r G$  vs Pressure Ratio

