Outline of Part 1: Thermo

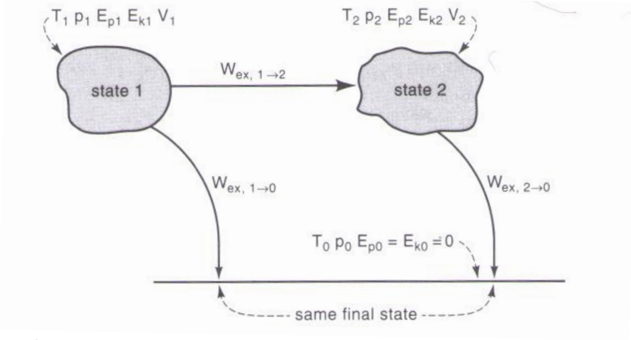
Objective: Derive and understand the physical laws that characterize and limit energy conversion systems

- 1st Law of Thermodynamics
  - Internal energy
  - Work
  - Enthalpy
- 2nd Law of Thermodynamics
  - Entropy
  - Reversible and irreversible processes
  - State functions
- Heat to work conversion
  - T-S diagrams
  - Idealized systems (Carnot cycle)
- Real heat to work and work to heat conversion systems
  - Rankine cycles
  - Refrigeration cycles and heat pumps
  - Engines
- **Exergy: calculating the maximum work that can be produced/recovered**
- Electrical systems
  - Electrical machines
  - Fuel cells

Exergy

Exergy (W_{ex}): the maximum amount of **useful** work obtainable for a given process (= a system going from state 1 to state 2).

For the calculation, we need: State 1, State 2 and the environment (State 0)

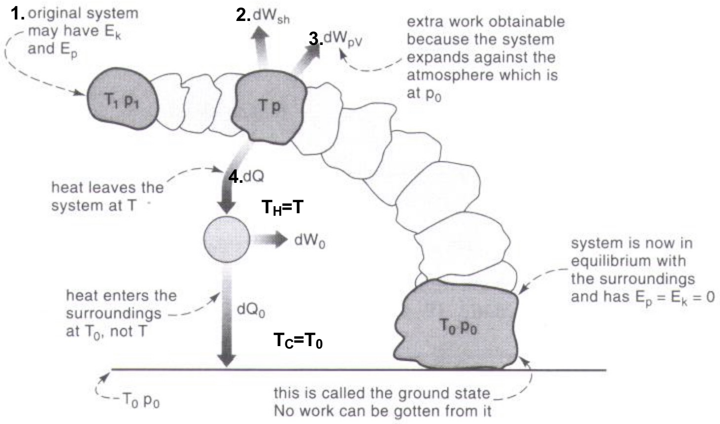


The exergy of this change is equal to the difference of the exergies of each state:

$$W_{ex,1\rightarrow 2} = W_{ex,2\rightarrow 0} - W_{ex,1\rightarrow 0}$$

Calculating ground state Exergy

All energy has to be accounted for as we bring our system to the ground state. This includes:



Is this just a Carnot Cycle? **No! E_p, E_k and dW_{sh} are included as well.**

Calculating ground state Exergy

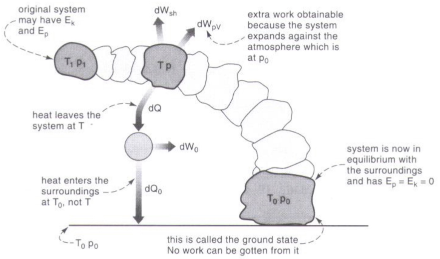
1st Law:

$$dE = dQ_0 - dW$$

Includes dU, dE_p and dE_k

Is the heat released to ground state

Includes all $dW = dW_{sh} + dW_{pV} + dW_0$



We know that the heat released by a Carnot engine is reversible and is at T_0:

$$dQ_0 = T_0 dS$$

$$dE = T_0 dS - dW_{sh} - dW_{pV} - dW_0 = T_0 dS - dW_{sh} - p_0 dV - dW_0$$

$$dW_{Ex} = dW_{sh} + dW_0 \quad = -dE + T_0 dS - p_0 dV$$

Calculating ground state Exergy

$$dW_{Ex} = -dE + T_0 dS - p_0 dV$$

We integrate (with $E_0 = U_0$) :

$$W_{Ex,1\to 0} = -(U_0 - E_1) + T_0(S_0 - S_1) - p_0(V_0 - V_1)$$

Assuming no changes in potential or kinetic energy:

$$W_{Ex,1\to 0} = -(U_0 - U_1) + T_0(S_0 - S_1) - p_0(V_0 - V_1)$$

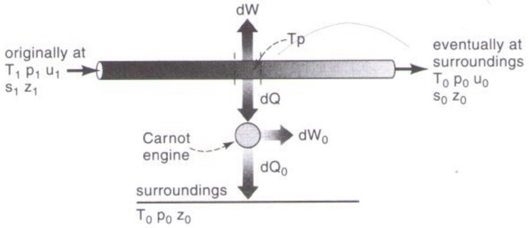
For a fuel that starts out at T_0 and P_0 (and *G=U-TS+PV*):

$$W_{Ex,1\to 0} = -\Delta G_0$$

For a change from State 1 to State 2:

$$W_{Ex,1\to 2} = W_{Ex,1\to 0} - W_{Ex,2\to 0} = -(E_2 - E_1) + T_0(S_2 - S_1) - p_0(V_2 - V_1)$$

Exergy in steady-state/flow systems



Starting with:

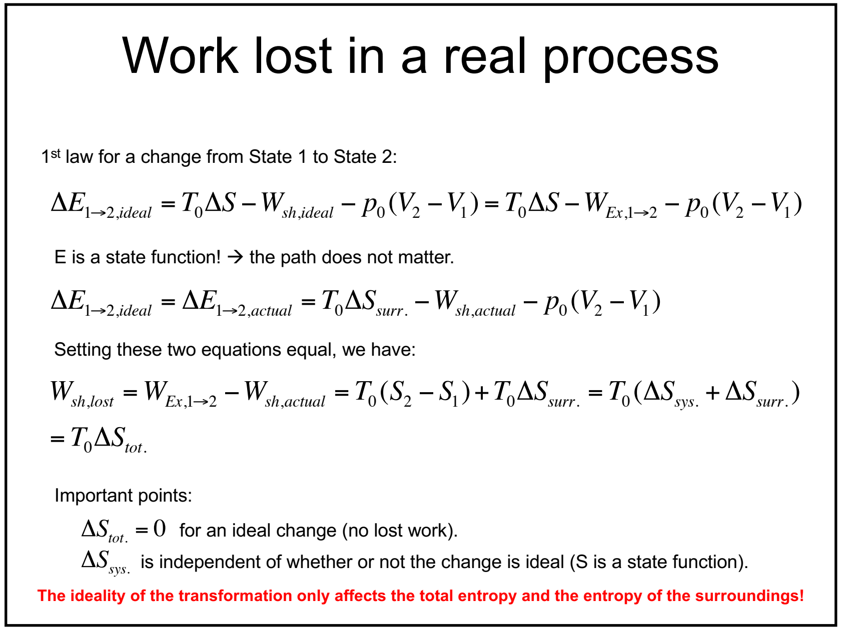
$$W_{Ex,1\to 0} = -(U_0 - U_1) + T_0(S_0 - S_1) - (p_0 V_0 - p_1 V_1)$$

By using enthalpy:

$$W_{Ex,1\to 0} = -(H_0 - \left[H_1 + E_p + E_k\right]) + T_0(S_0 - S_1)$$

Assuming that there is no change in kinetic and potential energy:

$$W_{Ex,1\to 2} = -(H_2 - H_1) + T_0(S_2 - S_1) = -\Delta G_0$$



Work lost in a real process

1st law for a change from State 1 to State 2:

$$\Delta E_{1\to 2,ideal} = T_0\Delta S - W_{sh,ideal} - p_0(V_2 - V_1) = T_0\Delta S - W_{Ex,1\to 2} - p_0(V_2 - V_1)$$

E is a state function! → the path does not matter.

$$\Delta E_{1\to 2,ideal} = \Delta E_{1\to 2,actual} = T_0\Delta S_{surr.} - W_{sh,actual} - p_0(V_2 - V_1)$$

Setting these two equations equal, we have:

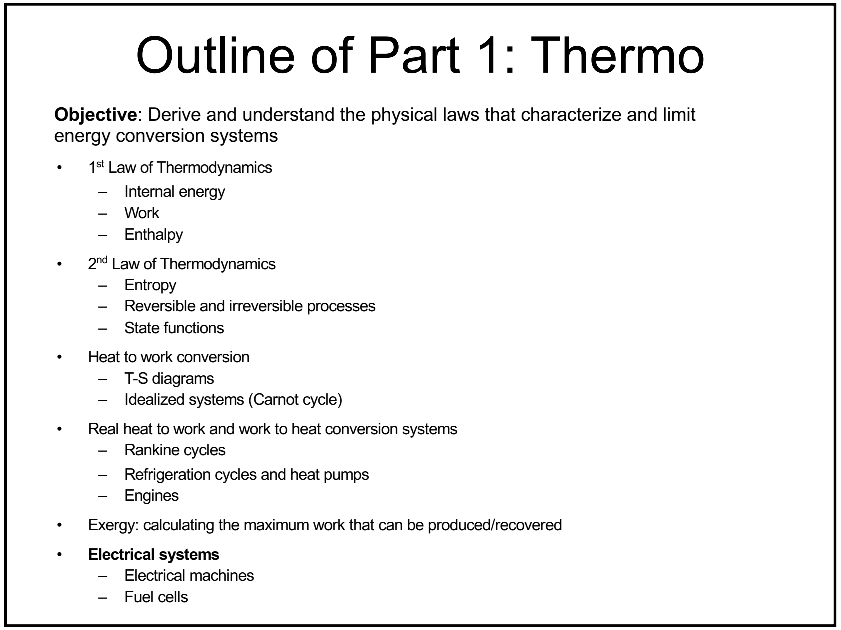
$$W_{sh,lost} = W_{Ex,1\to 2} - W_{sh,actual} = T_0(S_2 - S_1) + T_0\Delta S_{surr.} = T_0(\Delta S_{sys.} + \Delta S_{surr.})$$
$$= T_0\Delta S_{tot.}$$

Important points:

$\Delta S_{tot.} = 0$ for an ideal change (no lost work).

$\Delta S_{sys.}$ is independent of whether or not the change is ideal (S is a state function).

The ideality of the transformation only affects the total entropy and the entropy of the surroundings!



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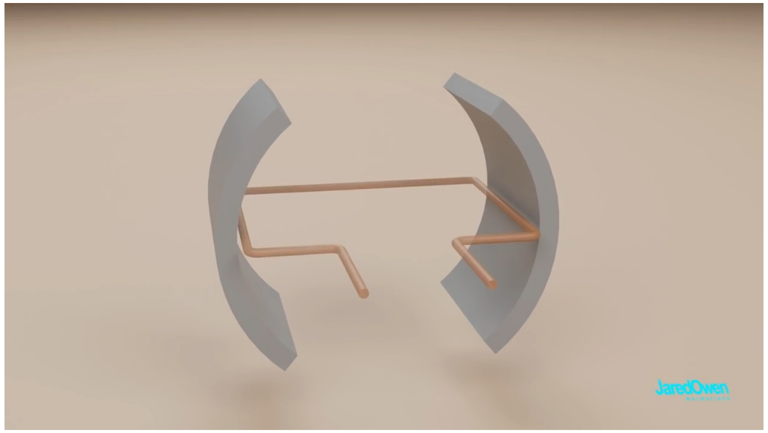
  - Fuel cells

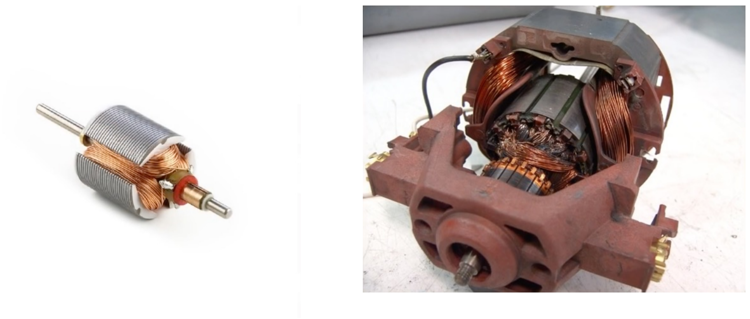
Electric motors

DC motors



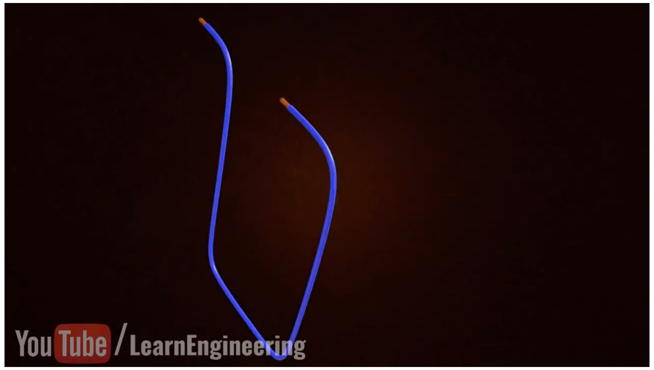
Electric motors

DC motors



Electric motors

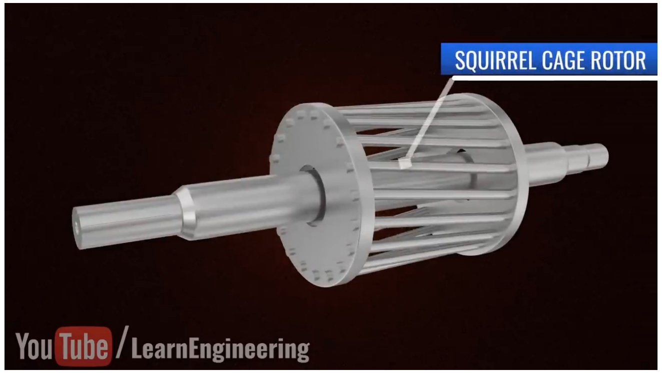
AC induction motors



146

Electric motors

AC induction motors



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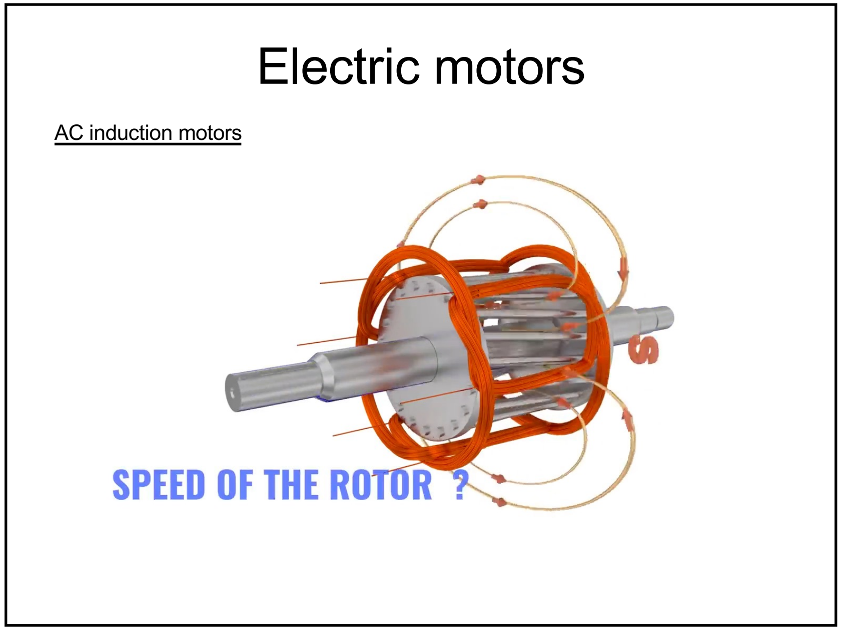
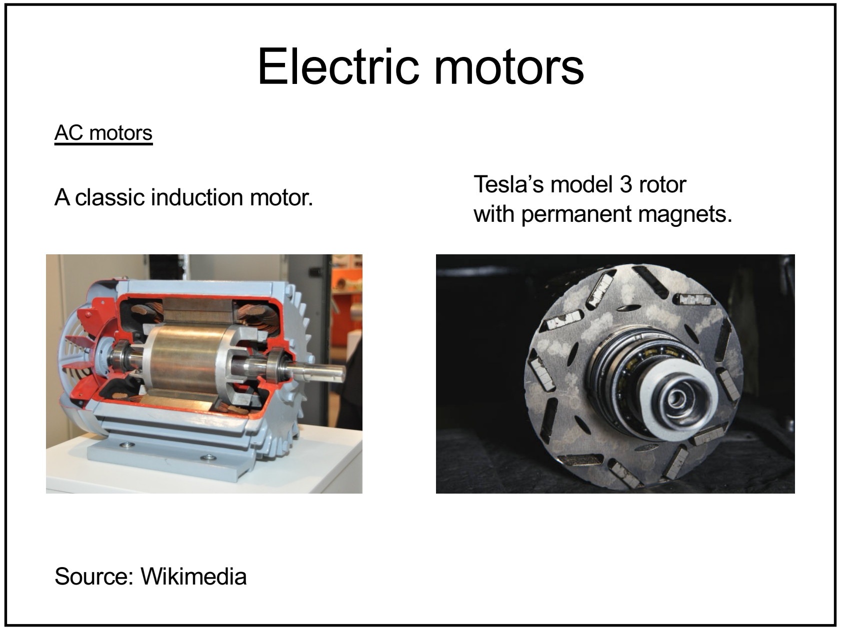


Electric motors

AC induction motors

SPEED OF THE ROTOR ?



Electric motors

AC motors

A classic induction motor.

Tesla’s model 3 rotor
with permanent magnets.

Source: Wikimedia

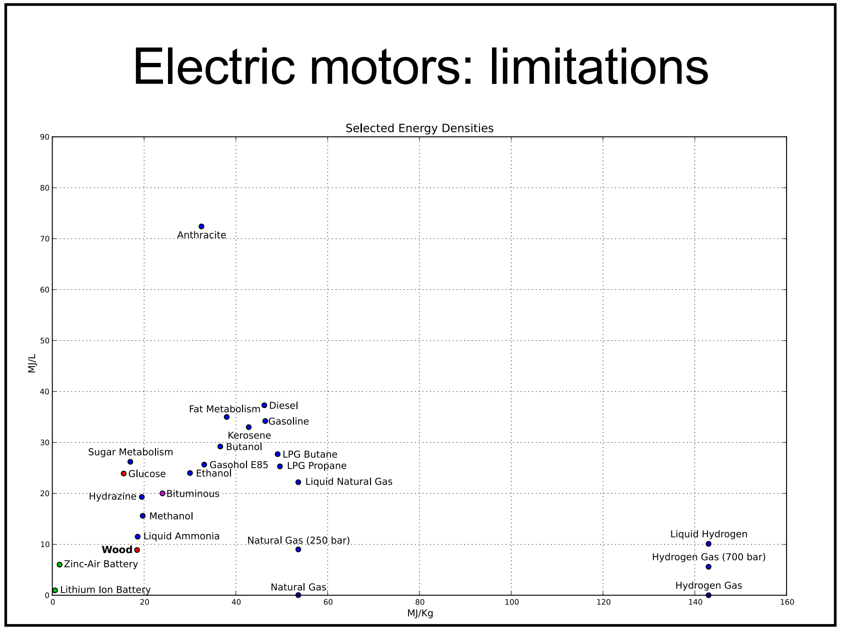
Electric motors

Due to the lack of friction or significant waste heat generated, electric motors are very efficient….

Typical efficiencies are usually above 90%.

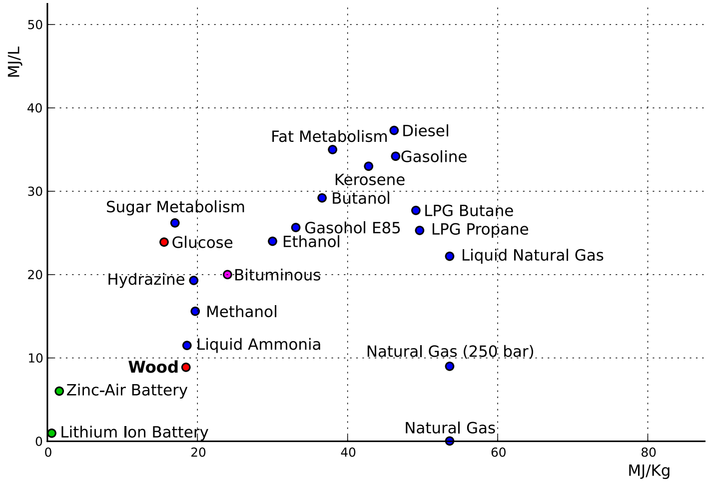
- Best AC induction motors have reached 94% efficiencies
- Tesla's AC permanent magnet Model 3 motor has reportedly reached 96% efficiencies

Why are we even considering other types of motors?



Electric motors: limitations

Electric motors: limitations



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Basics of fuel cells

The idea of fuel cells is to combine the energy density of fuels with electricity generation.

Fuel oxidation involves the exchange of electrons:

$$H_2 + \frac{1}{2} O_2 \rightleftharpoons H_2O$$

This reaction can be separated into two half reactions:

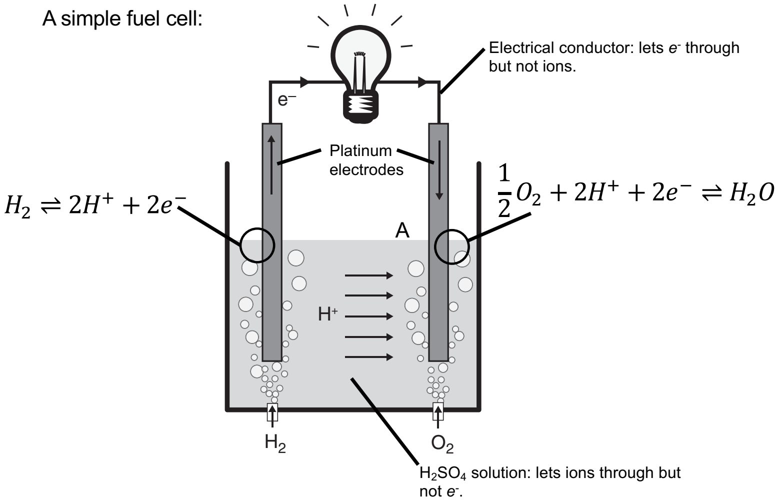
$$H_2 \rightleftharpoons 2H^+ + 2e^-$$

$$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$$

A fuel cells is made by spatially separating these two reactions and forcing the flux of electrons through a conductor to generate a current.

Basics of fuel cells

A simple fuel cell:



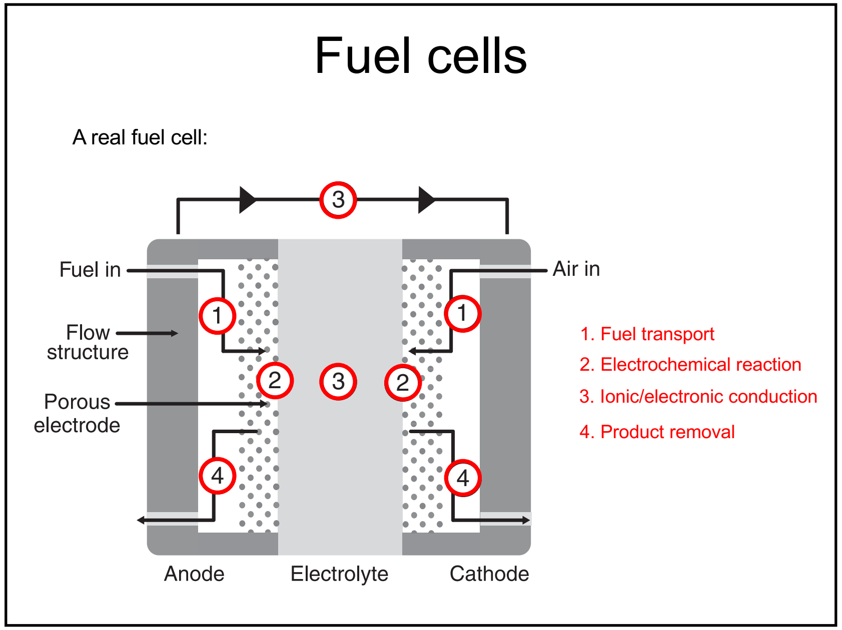
Electrical conductor: lets e^- through but not ions.

Platinum electrodes

$$H_2 \rightleftharpoons 2H^+ + 2e^-$$

$$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$$

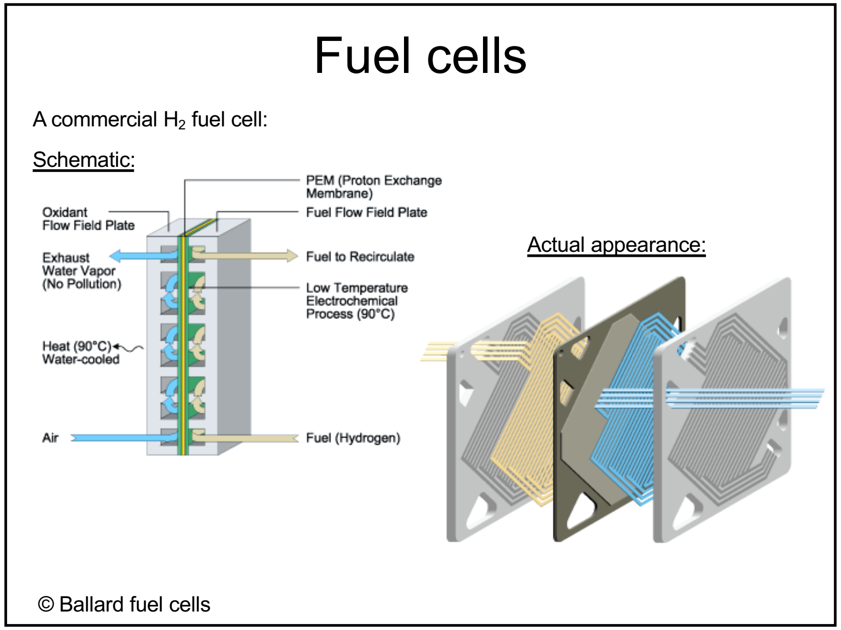
H_2SO_4 solution: lets ions through but not e^-.



Fuel cells

A real fuel cell:

1. Fuel transport
2. Electrochemical reaction
3. Ionic/electronic conduction
4. Product removal



Fuel cells

A commercial H_2 fuel cell:

Schematic:

Actual appearance:

© Ballard fuel cells

Thermodynamic potentials

Previously, we had explored the first law in an isolated system and expressed it as:

$$dU = TdS - PdV$$

Mathematically, we can understand this as describing *U* as a function of S and V:

$U(S,V)$ which, in a non isolated system would also depend on *N* (the total number of moles): $U(S,V,N)$

Thinking of U purely as a mathematical function depending on these variables, we can write:

$$dU(S,V,N) = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN$$

Comparing both definitions of U, we can write:

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_{S,N} = -P$$

Finally, the partial derivative of *U* by *N* is often defined as the chemical potential μ:

$$\left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu$$

Thermodynamic potentials

Measuring or describing *U* as a function of of entropy and volume is difficult in the lab:

$$dU = TdS - PdV$$

This:

Does not exist…

Thermodynamic potentials

Measuring or describing *U* as a function of of entropy and volume is difficult in the lab: $dU = TdS - PdV$

This:

Does exist!

In general extensive properties (which depend on the size of the system) are more difficult to change than intensive properties (that are independent of the size of the system)…

Thermodynamic potentials

Can we describe another thermodynamic potential (a state function that contains the same amount of mathematical information as *U*) that depends on simpler variables to modify?

A mathematical transformation exists that allows us to do this: Legendre transformations.

Starting with: $dU = TdS - PdV$

We use the differential of the variables we want to change and apply the chain rule: $d(PV) = PdV + VdP$

Rearranging: $-PdV = -d(PV) + VdP$

Which we can substitute into the definition of *dU*:

$$dU = TdS - d(PV) + VdP$$

Considering the variation of *U* with *N*: $dU = TdS - d(PV) + VdP + \mu dN$

Thermodynamic potentials

$$dU = TdS - d(PV) + VdP + \mu dN$$

Rearranging, we can make the definition of enthalpy appear:

$$d(U + PV) = dH = TdS + VdP + \mu dN$$

Enthalpy emerges from a mathematical transformation…

We can do a further transformation using de differential of *TS*:

$$d(TS) = TdS + SdT$$

Which rearranges to:

$$TdS = d(TS) - SdT$$

Applied to *dH*, we can get the definition of Gibbs free energy *(G):*

$$d(U + PV - TS) = dG = -SdT + VdP + \mu dN$$

Thermodynamic potentials

Starting with the original definition of *dU*:

$$dU = TdS - PdV$$

We can directly apply the transformation using *TS*:

$$d(TS) = TdS + SdT \quad \text{or} \quad TdS = d(TS) - SdT$$

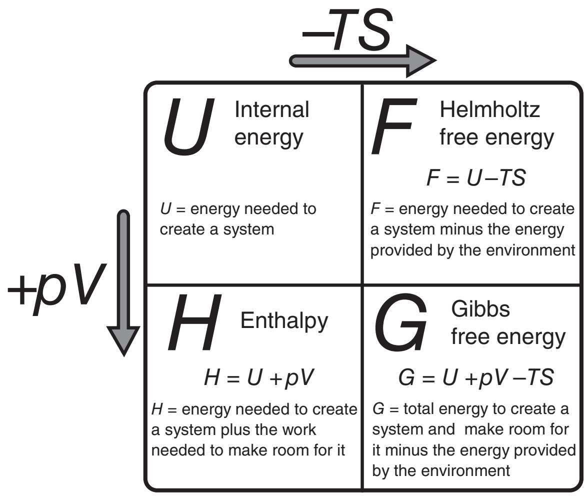
Which leads to the definition of Hemholtz energy (*F*):

$$d(U - TS) = dF = -SdT - PdV + \mu dN$$

PV can be interpreted physically as the work needed to create volume for the system to exist.

Similarly, *TS* can be interpreted as the energy required to be exchanged with the environment by the system.

Thermodynamic potentials



$-TS$

$+pV$

U Internal energy

U = energy needed to create a system

F Helmholtz free energy

$F = U - TS$

F = energy needed to create a system minus the energy provided by the environment

H Enthalpy

$H = U + pV$

H = energy needed to create a system plus the work needed to make room for it

G Gibbs free energy

$G = U + pV - TS$

G = total energy to create a system and make room for it minus the energy provided by the environment

Fuel cell efficiency

Let's rewrite the first law for fuel cells. In the case of the fuel cell, all non-PV work will end up as electrical work:

$$dU = dQ + dW_{electric} - dW_{PV}$$

In the best case, we will have:

$$dQ = dQ_{rev} = TdS$$

Which would lead to:

$$dU = TdS - dW_{electric} - PdV$$

Using the definition of free energy ($G = U + PV - TS$):

$$dG = dU - SdT - TdS + PdV + VdP = -SdT + VdP - dW_{electric}$$

Fuel cell efficiency

$$dG = -SdT + VdP - dW_{electric}$$

At constant T and P:

$$dG = -dW_{electric}$$

Therefore, in an ideal transformation for a given oxidation, we have:

$$W_{electric} = -\Delta G_{RXN}$$

With this result, we can now think of calculating an efficiency:

$$\eta = \frac{W_{electric}}{Total\ \ energy}$$

Assuming the input is the full calorific value of the fuel, the efficiency becomes:

$$\eta = \frac{-\Delta G_{RXN}}{-\Delta H_{RXN}}$$

Fuel cell efficiency

$$\eta = \frac{-\Delta G_{RXN}}{-\Delta H_{RXN}}$$

For example, if we take hydrogen oxidation:

$$H_2 + \frac{1}{2} O_2 \rightleftharpoons H_2O$$

$\Delta G_{RXN} = -237\ \text{kJ/mol}$

➡ 83%

$\Delta H_{RXN} = -286\ \text{kJ/mol}$

Fuel cell efficiency

$$\eta = \frac{-\Delta G_{RXN}}{-\Delta H_{RXN}}$$

This efficiency is not always appropriate to use. To understand why, let's introduce enthalpy in the definition of free energy:

$$G = U + PV - TS = H - TS \longrightarrow \Delta G = \Delta H - T\Delta S$$

$$\eta = \frac{-\Delta G_{RXN}}{-\Delta H_{RXN}} = \frac{\Delta H_{RXN} - T\Delta S_{RXN}}{\Delta H_{RXN}} = 1 - \frac{T\Delta S_{RXN}}{\Delta H_{RXN}}$$

For the rare cases where entropy is positive, we will have an efficiency over 100%!* → There must be something else!

$$\eta = \frac{W_{electric}}{Total\ \ energy} = \frac{W_{electric}}{Energy\ from\ RX + heat\ received}$$

$$\frac{-\Delta G_{RXN}}{-\Delta H_{RXN} + T\Delta S_{RXN}} = \frac{\Delta H_{RXN} - T\Delta S_{RXN}}{\Delta H_{RXN} - T\Delta S_{RXN}} = 1$$

In cases where heat is being received from the surroundings, this should be included in the efficiency and, by definition, the maximum efficiency will be 100%.

*A fuel oxidation's enthalpy will always be negative, otherwise it will not be a fuel…

Fuel cells: reversible voltage

The electric work of moving a charge *q* is proportional to the voltage or electrical potential (*E*):

$$W_{electric} = qE$$

When such a charge is carried by electrons, we have:

$$q = nF$$

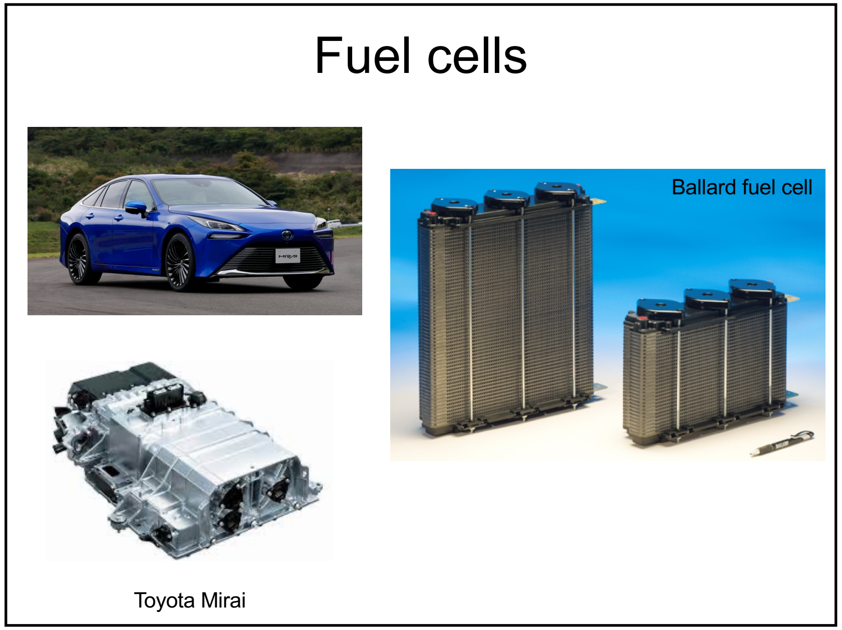
Number of moles of electrons

Faraday's constant

Since we have: $W_{electric} = -\Delta G_{RXN}$

We can calculate the maximum reversible voltage for a single fuel cell:

$$E^0 = -\frac{\Delta G^0_{RXN}}{nF}$$



Fuel cells

Ballard fuel cell

Toyota Mirai