

# The Challenge of Water: A Tutorial on Thermodynamics

David Cahill, Professor and Department Head,  
Materials Science and Engineering,  
U. Illinois at Urbana-Champaign

World Materials Summit

October 9 , 2011

Many thanks to Profs. Mark Shannon



*water*CAMPUS

# Water and Energy are Interdependent

*Energy and power production require water:*

- Thermoelectric cooling
- Hydropower
- Fuel Production (fossil fuels, H<sub>2</sub>, biofuels)
- Emission control
- CO<sub>2</sub> separation and sequestration

*Water production, processing, distribution, & end-use require energy*

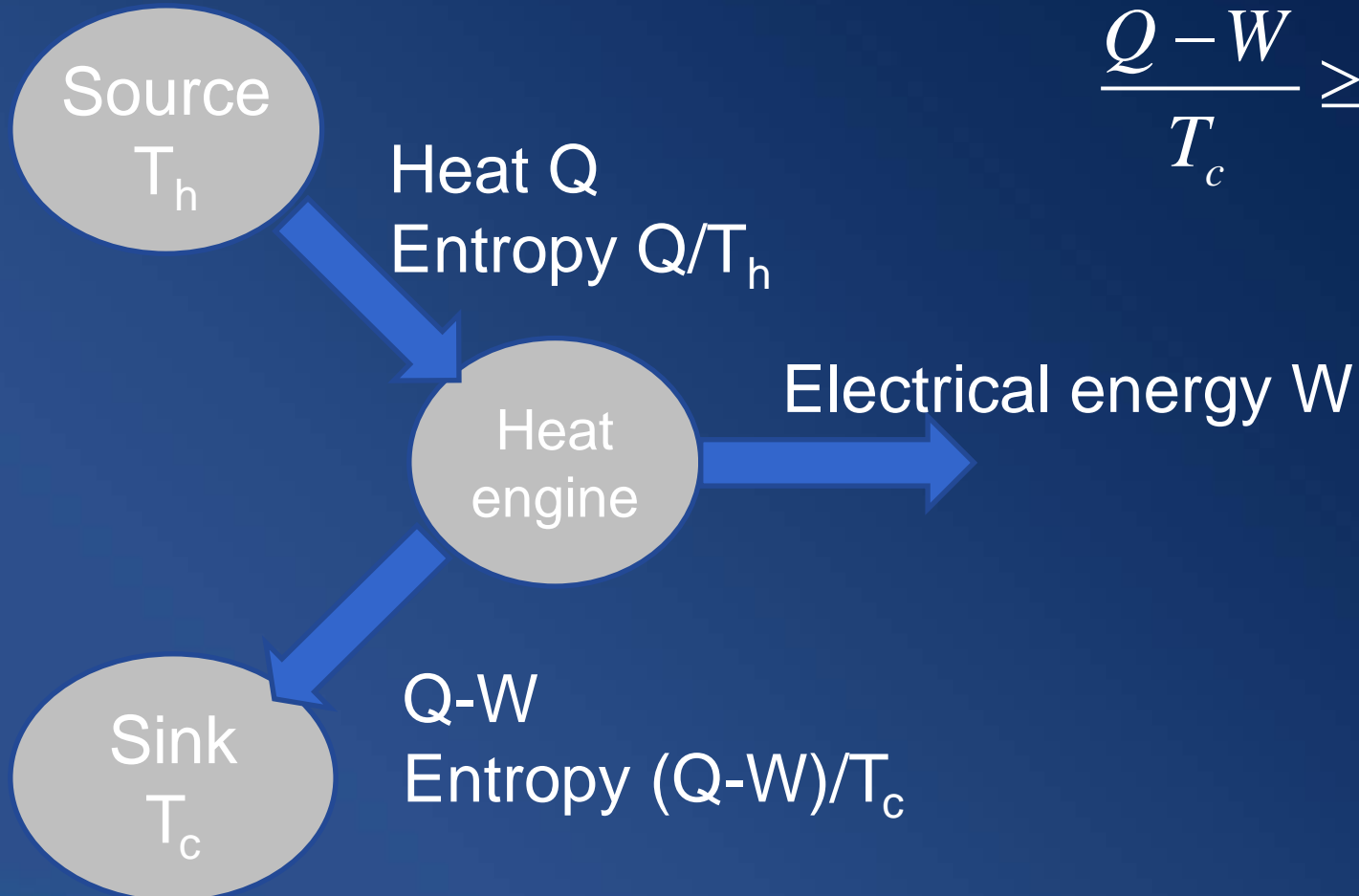
- Pumping
- Conveyance
- Treatment



Dr. Michael Hightower, Sandia National Labs, 2010



# Second Law of Thermodynamics



$$\frac{Q-W}{T_c} \geq \frac{W}{T_h}$$



# Second Law of Thermodynamics

$$\frac{Q - W}{T_c} \geq \frac{Q}{T_h} \quad W \leq \left(1 - \frac{T_c}{T_h}\right) Q$$

- 💧 In typical steam cycles (coal, nuclear) heat flow into cold heat sink is approximately the same as electrical power  $(Q - W) \approx W$  (and comparable to heat lost to exhaust)
- 💧 Need to dissipate  $W$  of heat at as low of a temperature as possible.



# Cooling requirements in power generation

- 💧 Most effective way to do this is with water, either by heating a large volume by a small amount and then discharge to environment, or by evaporation.
- 💧 Discharge is warm and increases evaporation so overall consumption of water is similar in both cases.



# Cooling requirements in power generation

- 💧 Heat of vaporization of water is  $2 \text{ J/mm}^3$  or  $2 \text{ GJ/m}^3$
- 💧 In other words, need to evaporate  $0.5 \text{ m}^3$  of water per second for a 1 GW nuclear power plant.
- 💧 Order of magnitude the same as the household water use (in the US) of a small city of 100,000 (e.g., Champaign-Urbana, IL)



# Why not use more air cooling?

- Volume of air involved is huge.
  - Heat capacity per molecule is  $(7/2)k_B$
  - Heat capacity per unit volume is  $(7/2)(P/T) \approx 1 \text{ kJ/m}^3\text{-K}$  at ambient conditions
  - With  $\Delta T = 10 \text{ K}$ , requires nearly  $10^5$  more volume of air than evaporating water.
  - Enormous heat exchangers, fans, high capital costs.



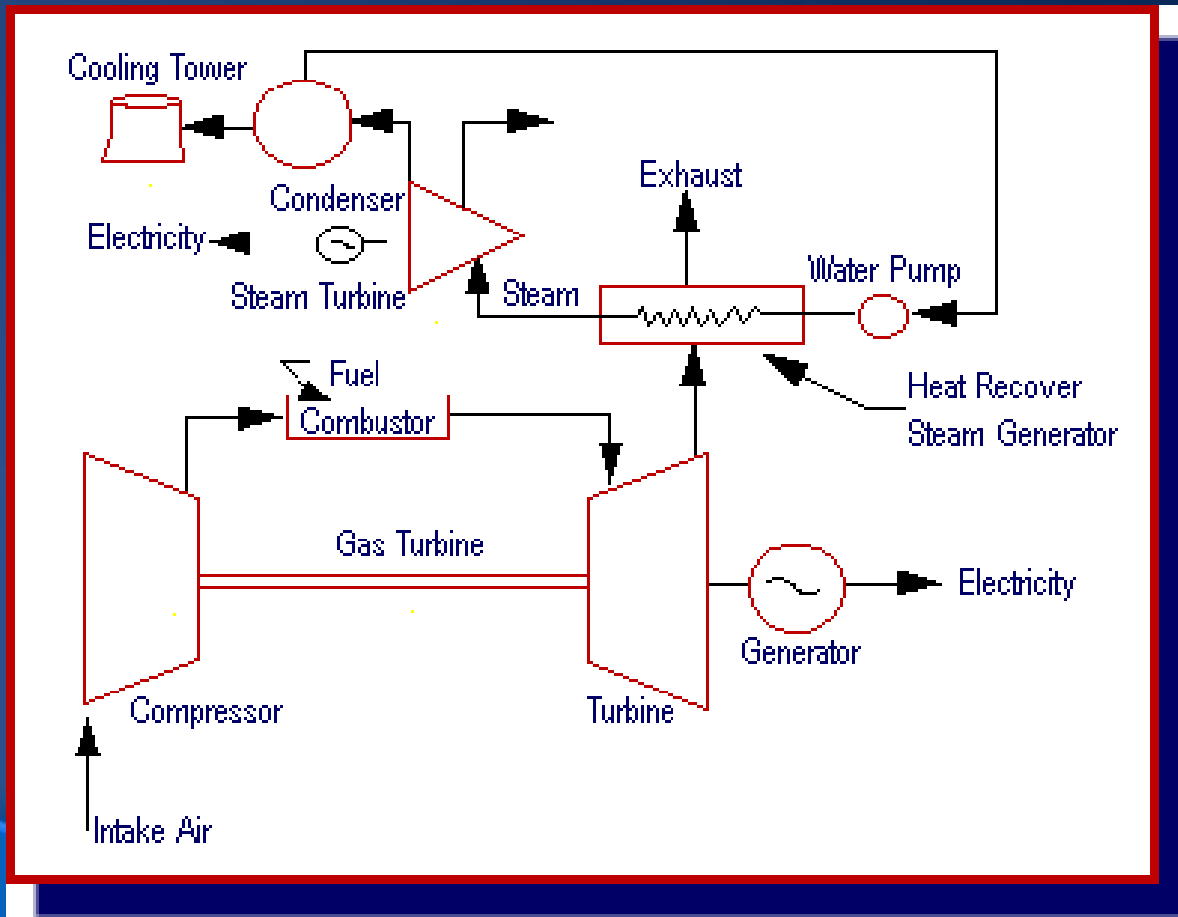
# Why not use more air cooling?

- 💧 Efficiency suffers: 0.1% per degree C.
  - 💧 Air temperature is not always as cold as available water. Worse in hot/climates where more air-conditioning is needed.
  - 💧 Additional thermal resistance because heat transfer is not as effective: basic property of effusivity (square root of the product of thermal conductivity and heat capacity per unit volume) is smaller by a factor of 100.
- 💧 Trade-off: do you want to reduce use of H<sub>2</sub>O or CO<sub>2</sub> emission?

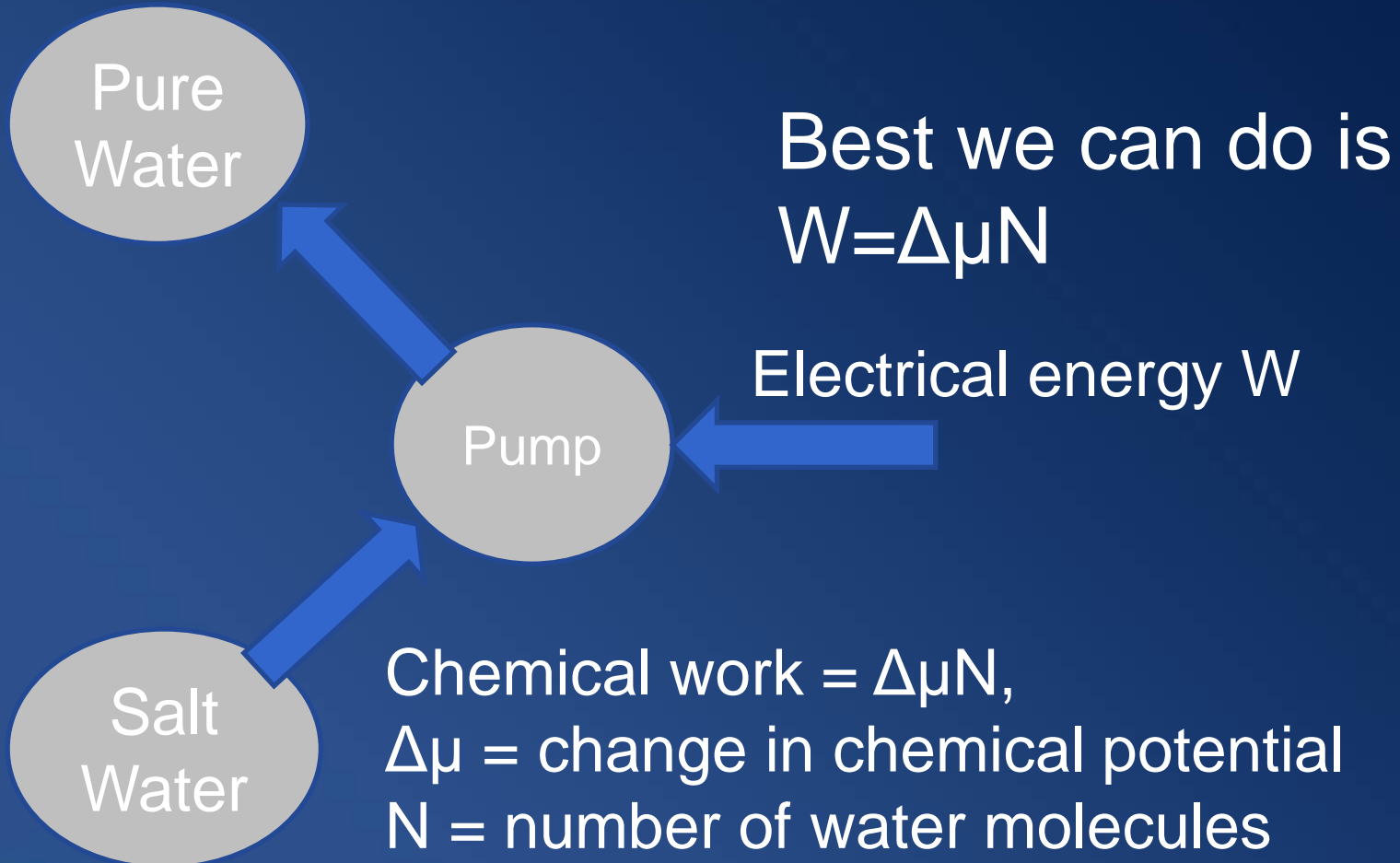


# Why not use more air cooling?

- Combined cycle (natural gas powered) saves water and reduces CO<sub>2</sub> relative to coal.

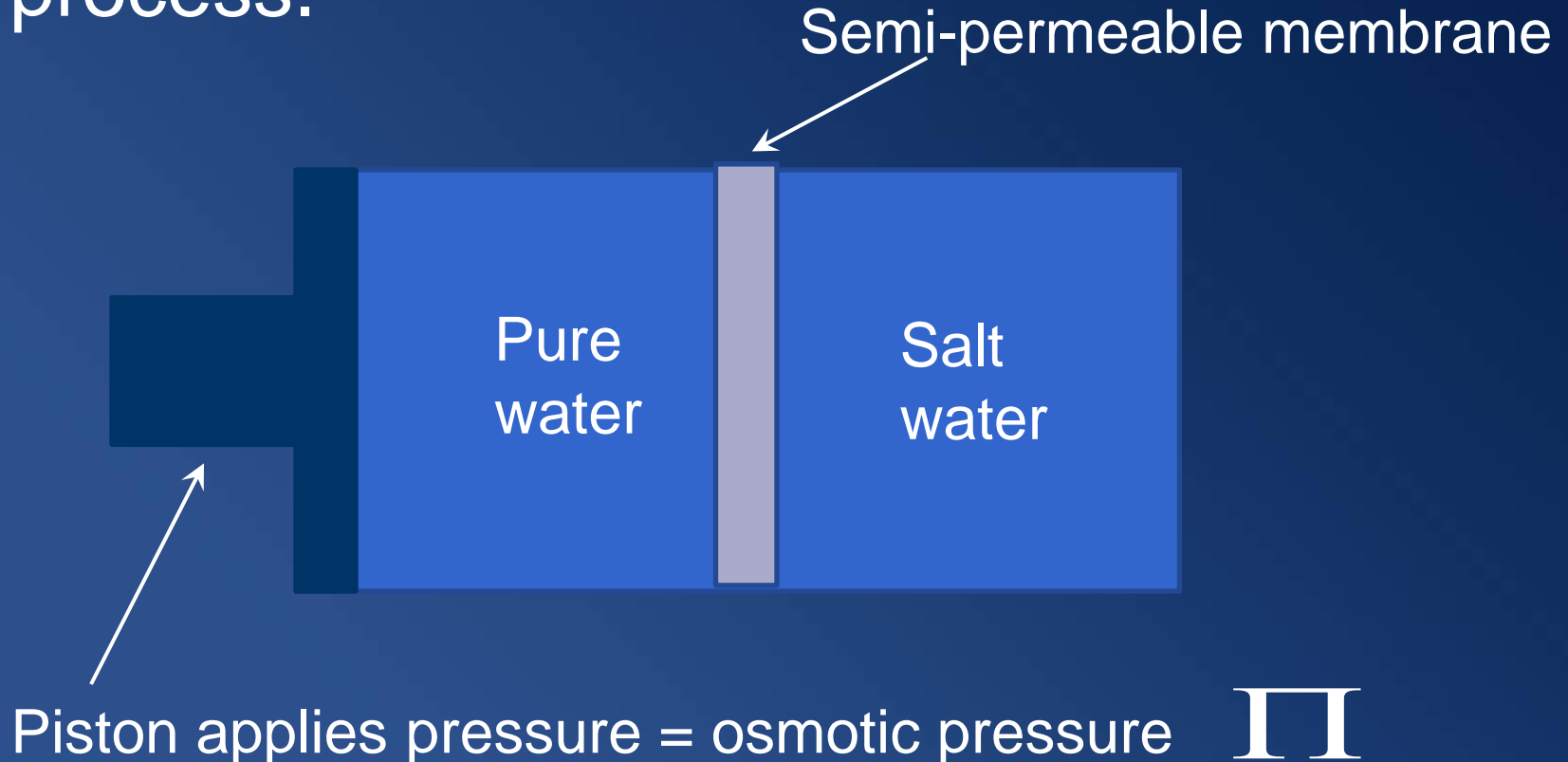


# Thermodynamics of water purification



# Thermodynamics of water purification

- Lowest possible energy is for a reversible process.



# Thermodynamics of water purification

- For ideal solution of  $n$  ions per unit volume

$$\Pi = nk_B T$$

- Differential work done in moving volume  $dV$

$$dW = \Pi(dV)$$

- Integrate from initial to final osmotic pressure (assume 50% recovery)

$$W = k_B T \int_{V_0}^{(1/2)V_0} n \left( \frac{V_0}{V} \right) dV$$



# Thermodynamics of water purification

- For 50% recovery, ideal solution, 3.5% by mass NaCl ( $V_0 = 2 \text{ m}^3$  to recover  $1 \text{ m}^3$  pure water)

$$W = nV_0k_B T \ln(2)$$

$$W = 3.8 \text{ MJ} \approx 1 \text{ kWh}$$

- No process can do better than this at 50% recovery. (For 0% recovery, no  $\ln(2)$  term.)
- State-of-the-art RO is only a factor of 2 higher than this limit.



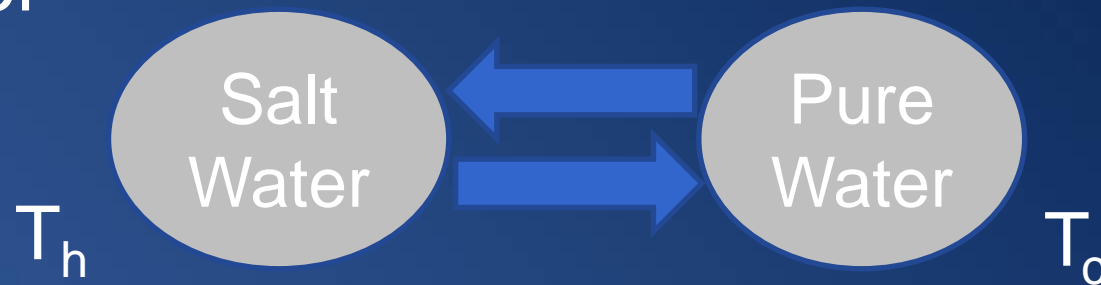
# Is 1 kWh = 3.6 MJ a lot of energy?

- 💧 Electrical power cost is about \$0.10
- 💧 Heat 10 L of water to boiling point
- 💧 Light a CF light bulb for a few days
- 💧 Run a refrigerator for ½ day
- 💧 Do 3600 google searches
  - 💧 One google search consumes as much energy as state-of-the-art RO uses to purify a small cup of water.



# Thermodynamic limits for a distillation process are the same

- For a reversible process, we have to make the vapor pressures equal (almost) but that means the temperature of the salt water is higher



Approximate heat input: 
$$dQ = \Delta H \left( 1 - \frac{T_c}{T_h} \right) dV$$

$\Delta H$ =enthalpy of vaporization  
per unit volume



# Thermodynamic limits for distillation

- Real-world distillation processes (multi-stage) work far from the thermodynamic limit.

$$dW = \Delta H \left( 1 - \frac{T_c}{T_h} \right) dV$$

- Even for  $\Delta T=10$  K, this is 15 times worse than the thermodynamic limit.



# But maybe sometimes heat is free, i.e., “waste heat”?

- Low-grade (low temperature) heat source that is not feasible to use in electrical power generation might be used to purify water.
- But keep in mind that high efficiency power generation uses low temperature heat sinks. Not much of the heat is “wasted”

