The Challenge of Water: A Tutorial on Thermodynamics

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Water and Energy are Interdependent

Energy and power production require water:

• Thermoelectric cooling
• Hydropower
• Fuel Production (fossil fuels, H₂, biofuels)
• Emission control
• CO₂ 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

\[ \frac{Q - W}{T_c} \geq \frac{W}{T_h} \]

- **Source** $T_h$
  - Heat $Q$
  - Entropy $Q/T_h$
- **Heat engine**
- **Sink** $T_c$
  - Q-W
  - Entropy $(Q-W)/T_c$
  - Electrical energy $W$
Second Law of Thermodynamics

\[ \frac{Q - W}{T_c} \geq \frac{Q}{T_h} \quad \text{and} \quad W \leq \left(1 - \frac{T_c}{T_h}\right)Q \]

- 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 a 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 H₂O or CO₂ emission?
Why not use more air cooling?

- Combined cycle (natural gas powered) saves water and reduces CO$_2$ relative to coal.
Thermodynamics of water purification

**Pure Water**

Best we can do is

\[ W = \Delta \mu N \]

**Salt Water**

Chemical work = \( \Delta \mu N \),  
\( \Delta \mu = \) change in chemical potential  
\( N = \) number of water molecules

**Pump**

Electrical energy \( W \)
Thermodynamics of water purification

- Lowest possible energy is for a reversible process.

Semi-permeable membrane

Piston applies pressure = osmotic pressure

Pure water

Salt water

Π
Thermodynamics of water purification

- For ideal solution of $n$ ions per unit volume
  \[ \Pi = nk_B T \]
- Differential work done in moving volume
  \[ dW = \Pi (dV) \]
- 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”