ESCI 341 – Atmospheric Thermodynamics
Lesson 11 – The Second Law of Thermodynamics

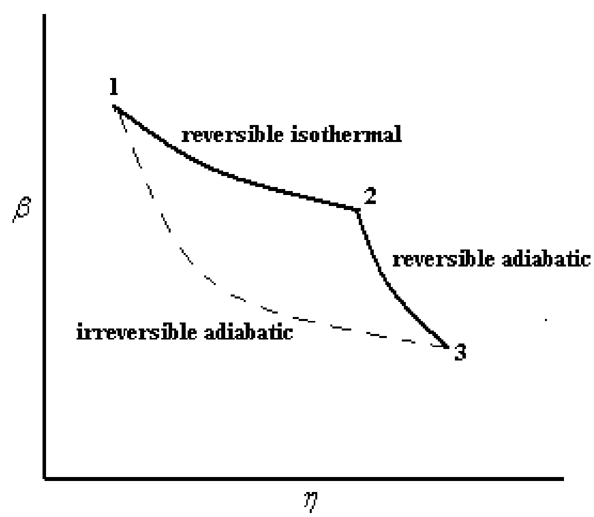
References: *Physical Chemistry (4th edition)*, Levine
Thermodynamics and an Introduction to Thermostatistics, Callen

THE SECOND LAW OF THERMODYNAMICS

- **There are two common ways of stating the Second Law of Thermodynamics.**
  - ***Statement #1*: "In an isolated system, entropy never decreases ($\Delta S_{isol} \geq 0$)."**
  - ***Statement #2*: "*It is impossible for a system to undergo a cyclic process whose sole effects are the flow of heat into the system from a heat reservoir and the performance of an equivalent amount of work by the system on the surroundings.*"**
- **Statement #2 is called the Kelvin-Planck statement, and asserts that you cannot convert a given amount of heat into an equal amount of work (there is no such thing as a 100% efficient engine.)**
- **Even though the two statement look very different, they are actually equivalent!**

PROOF THAT *STATEMENT #1* AND *STATEMENT #2* ARE EQUIVALENT

- **Imagine the cyclic process shown on the thermodynamic diagram below, where β and η are arbitrary thermodynamic variables.**



  - ***Leg 1*: A reversible, isothermal process from State 1 to State 2. The change in entropy of this process is**

$$\Delta S_1 = Q_{rev}/T \quad \textbf{(1)}$$

- **o** ***Leg 2*: A reversible, adiabatic process to State 3 (there is no change in entropy during this process).**
- **o** ***Leg 3*: An irreversible, adiabatic process back to State 1. The entropy change during this leg we will call ΔS_3.**

- **Since entropy is a state variable, and since we end up at the same point as we started, the total entropy change of the cycle must be zero. Therefore, we have**

$$\Delta S_3 = -\Delta S_1 = -Q_{rev}/T \,. \qquad \textbf{(2)}$$

- **We also know that, since internal energy is a state variable, then**

$$\Delta U = Q_{rev} + W = 0 \,. \qquad \textbf{(3)}$$

  - **o This means that the work done in the cyclic process is equal in magnitude, but of opposite sign, to the heat added to the system,**

$$W = -Q_{rev} \,. \qquad \textbf{(4)}$$

- **If Q_{rev} were positive (meaning heat is added to the system), the work would be negative. This means the system would do work on the surroundings.**
  - **o The net result of this would be a cyclic process in which all the heat added to the system is converted into work, <u>which violates the Planck statement</u>.**
  - **o Therefore, Q_{rev} must be negative.**
  - **o A negative Q_{rev} doesn't violate the Planck statement, since in this case work is being done on the system, and heat is being extracted. This is perfectly allowed by the Planck Statement, as work can be converted to heat with 100% efficiency. The Planck statement says that you can't convert heat to work with 100% efficiency, but you <u>are</u> allowed to convert work to heat with 100% efficiency.**

- **We've proven that $Q_{rev} < 0$. This means, from Eq. (2), that**

$$\Delta S_3 = -Q_{rev}/T > 0 \,. \qquad \textbf{(5)}$$

  - **o Thus, <u>*the entropy must increase in an irreversible, adiabatic process*</u>.**

- **If a system is isolated, it is adiabatic. Therefore, <u>in an isolated system, any irreversible process will result in an increase in the total entropy of the system</u>.**
  - **o Purely reversible processes in an isolated system will leave the entropy unchanged.**

- **The entire universe is an isolated (and closed) system (at least as far as we know). Therefore, we can also write**

$$\Delta S_{universe} \geq 0\,.$$

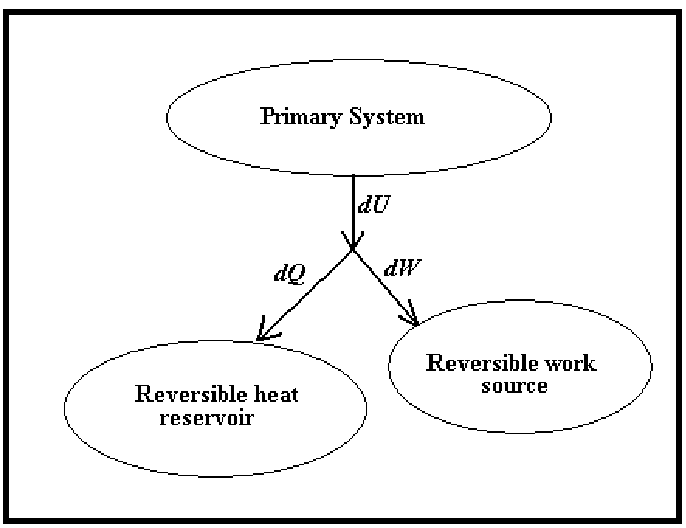
- **We've just proven that the mathematical statement, $\Delta S_{isol} \geq 0$, and the Kelvin-Planck statement, are equivalent!**

FURTHER COMMENTS ON THE SECOND LAW

- **Some things to remember:**
  - **In <u>any</u> irreversible, adiabatic process, entropy increases. This is true, even if the process is quasi-static.**
  - **In <u>any</u> reversible, adiabatic process, entropy remains constant.**
  - **In an isolated system, reversible processes don't change the total entropy of the system.**
  - **In an isolated system, irreversible processes always increase the total entropy of the system.**
  - **The entropy in an isolated system can never decrease. It can only remain constant (if the processes are purely reversible) or increase (if there are any irreversible processes).**
  - **The universe is an isolated system (so we believe): Since there are certainly lots of irreversible processes at play in our universe, then the total entropy of the universe is always increasing.**
- **The second law of thermodynamics is a big downer! It says we will never be able to construct a 100% efficient heat engine, or have a perpetual motion machine.**
- **Philosophical note: The second law of thermodynamics, like the first law, has never been proven to be true. In fact, it cannot be proven to be true. It is a 'principle' or 'law' that so far has always worked. But, that's not to say that at some point in time a process or phenomenon will be discovered that violates the second law of thermodynamics. In that event, then the second law will be proven to be false.**

THE MAXIMUM WORK THEOREM

- **The second law of thermodynamics tells us that there is no such thing as a 100% efficient heat engine (one that can consume a given amount of thermal energy and convert it completely into work).**
- **We can use the second law of thermodynamics to investigate the maximum theoretical efficiency of a heat engine.**
  - **This is not just an abstract idea for meteorologists. Many meteorological phenomenon, such as tropical cyclones, behave like heat engines, converting thermal energy into work (kinetic energy). We can therefore speak of the maximum theoretical efficiencies of tropical cyclones, the Hadley circulation, etc.**
- **Imagine an isolated thermodynamic system that consists of three subsystems:**
  - ***The primary system*: This subsystem undergoes a process between two thermodynamic states (State A and State B) and makes available an amount of energy *dU*.**
  - ***The reversible work source*: This subsystem either performs work, or has work performed on it.**
  - ***The reversible heat reservoir*: This subsystem is a repository for any residual heat.**



- **From the first law of thermodynamics we have**

$$dU = dQ + dW\,.$$

- **The total change in entropy of the entire system is the sum of the entropy changes of each individual subsystem, which is**

$$dS_{total} = dS_{primary} + dQ/T_r$$

where T_r is the temperature of the reversible heat reservoir.

- **Eliminating dQ from the two expressions above yields**

$$dW = dU + T_r dS_{primary} - T_r dS_{total}\,.$$

  - **In the expression above, the following are fixed: dU, $dS_{primary}$, and T.**

- **In order to achieve maximum efficiency, we want to maximize dW. To do this, we need to minimize dS_{total}. Ideally, we want to make $dS_{total} = 0$, which would occur if the system operates completely reversibly.**

- **We have just proven what is known as the *Maximum Work Theorem*: "*For all processes leading from a specified initial state to a specified final state of the primary system, the delivery of work is maximum (and the delivery of heat is minimum) for a reversible process. Furthermore, the delivery of work (and of heat) is identical for every reversible process.*"[1]**

MAXIMUM EFFICIENCY OF A HEAT ENGINE

- **We can use the maximum work theorem to determine the maximum theoretical efficiency of a heat engine. You might ask why we would be interested in studying heat engines in an atmospheric thermodynamics class. The answer is simple…many meteorological process (thunderstorms, hurricanes, extratropical cyclones, etc.) act as heat engines, converting thermal energy into kinetic energy (or work).**

- **A heat engine is an engine that takes heat from a hot reservoir, converts part of this heat into work, and deposits the remainder into a cold reservoir.**
  - **We will imagine that the hot and cold reservoirs are so large that their temperatures remain practically constant.**

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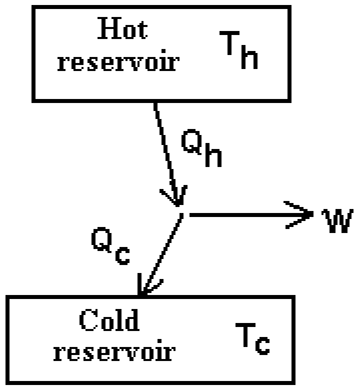
[1] *Thermodynamics and an Introduction to Thermostatistics*, Callen, 1985, John Wiley & Sons



- **From the first law of thermodynamics (conservation of energy) we have**

$$Q_h = W + Q_c.$$

- **The thermodynamic efficiency of the engine is defined as W/Q_h, and is**

$$\eta = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}.$$

- **The change in entropy is**

$$\Delta S = -\frac{Q_h}{T_h} + \frac{Q_c}{T_c}.$$

  Since we know the most efficient engine possible is a completely reversible engine (for which $\Delta S = 0$), we can write

$$\frac{Q_c}{Q_h} = \frac{T_c}{T_h}.$$

  - **Substituting the above expression into the equation for efficiency gives**

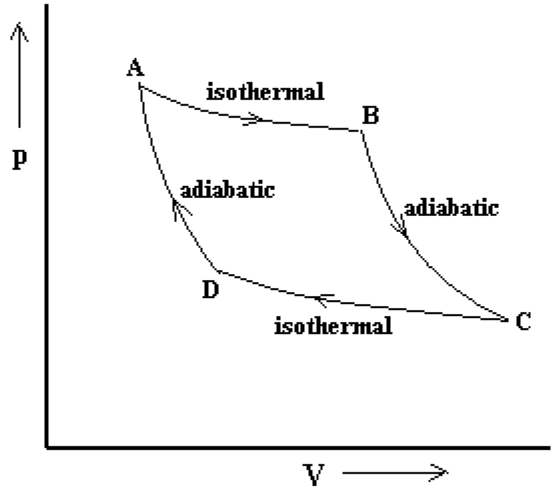
$$\eta = 1 - \frac{T_c}{T_h}.$$ ***Maximum theoretical efficiency of a heat engine***

- **The greater the temperature differences between the hot and cold reservoirs, the greater the efficiency.**
- **No real engine can ever be more efficient than a reversible engine. This means that the maximum efficiency of any heat engine is**

$$\eta_{real\,engine} \le 1 - \frac{T_c}{T_h}.$$

THE CARNOT CYCLE

- **The maximum work theorem, and the maximum efficiency of a heat engine were both derived without using any one specific reversible cycle (since it turns out that all reversible cycles have the same efficiency). However, most thermodynamics texts and discussions make reference to a specific reversible cycle known as the Carnot cycle, and historically the maximum work theorem and even the concept of entropy were developed using the Carnot cycle. Because of its historical significance we briefly discuss this cycle here.**
- **The Carnot cycle consists of four legs:**
    - **A high-temperature isothermal expansion, which requires an amount of heat to be added to the gas.**
    - **An adiabatic expansion.**
    - **A low-temperature isothermal contraction, which requires the removal of heat.**
    - **An adiabatic compression back to the original starting point.**
- **On a P-V diagram the Carnot cycle looks like**



APPLICATIONS OF HEAT-ENGINE EFFICIENCY TO THE ATMOSPHERE

- **At this point you may be asking "What in the heck does the efficiency of a heat engine have to do with atmospheric thermodynamics?" This is certainly a valid question. But it turns out that studying heat-engine efficiency is very relevant to atmospheric processes.**

- **Tropical cyclones, the Hadley circulation, monsoons, etc. can all be thought of as heat engines that operate between a high temperature reservoir (the Tropical oceans) and a low temperature reservoir (the upper troposphere), and convert the heat into kinetic energy.**
- **A knowledge of the 'efficiency' of these heat engines can allow us to place upper limits on the amount of kinetic energy that can be produced.**
- **However, atmospheric heat engines, like other real-life heat engines, are not reversible. To extend the concept of heat engines to real-life situations requires us to use the concept of nonequilibrium thermodynamics, or at least finite-time thermodynamics. Although these are beyond the scope of this course, a few good references or articles to read on this subject are**
    - **'Efficiency of a Carnot engine at maximum power output', F.L. Curzon and B. Ahlborn, *American Journal of Physics*, 43, pp. 22-24, 1975**
    - **'Wind energy as a solar-driven heat engine: A thermodynamic approach', J.M. Gordon and Y. Zarmi, *American Journal of Physics*, 57, pp. 995-998, 1989**
    - **'A nonendoreversible model for wind energy as a solar-driven heat engine', *Journal of Applied Physics*, 80, pp. 4872-4876, 1996**
    - ***Understanding Non-equilibrium Thermodynamics*, G. Lebon, D. Jou, and J. Casas-Vazquez, Springer-Verlag, 325 pp., 2010**

POTENTIAL TEMPERATURE

- **Potential temperature is defined as the temperature that an air parcel would have if it were brought adiabatically and reversibly to some reference pressure (almost always 1000 mb).**
- **From the Poisson relation involving *T* and *p*, we have**

$$Tp^{\frac{1-\gamma}{\gamma}} = Tp^{-R'/c_p} = const.$$

so that potential temperature can be written as

$$\theta = T\left(\frac{p_0}{p}\right)^{R'/c_p}.$$

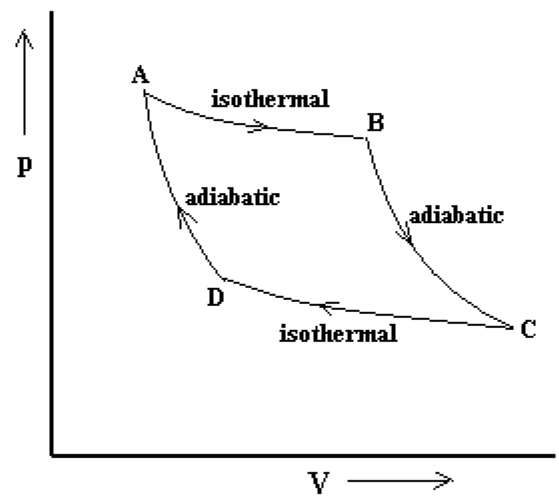
- **Potential temperature is conserved during a reversible adiabatic process. Therefore, it can be used as a proxy for entropy. In fact, the two are related via**

$$s = s_0 + c_p \ln\left(\frac{\theta}{T_0}\right).$$

- **Meteorologists often refer to adiabats as *isentropes*. Isentropic analysis is analysis done on surfaces of constant potential temperature.**

EXERCISES

1. An engine operates on a Carnot cycle. The working fluid is Helium, and ideal gas with a molecular weight of 4 g/mol. The initial pressure and specific volume are 1000 mb and 6 m^3/kg.



a. What is the initial temperature?

b. The volume at point B is 5 times greater than at point A. What is the pressure at point B?

c. The volume at point C is 5 times greater than at point B. What is the pressure at point C?

d. What is the temperature at point C?

e. What is the pressure and specific volume at point D?

f. What is the heat per unit mass added to the working fluid during the high temperature expansion (A to B)?

g. What is the heat per unit mass removed from the working fluid during the low temperature compression (C to D)?

h. What is the specific work (work per unit mass) done by the working fluid during one cycle?

i. Using your answers to f., g., and h., find the efficiency of this engine and compare it to the maximum theoretical efficiency given by

$$\eta = 1 - \frac{T_c}{T_h}.$$

2. Show that the maximum theoretical efficiency of a refrigerator (defined as the amount of heat removed from the cold reservoir divided by the work) is

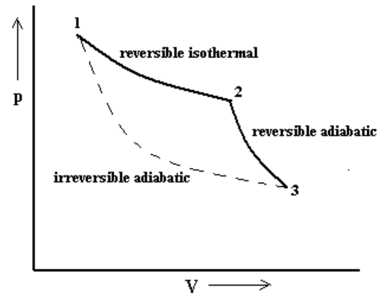
$$\eta = \frac{T_c}{T_h - T_c}.$$

3. Show that specific entropy is related to potential temperature via

$$s = s_0 + c_p \ln\left(\frac{\theta}{T_0}\right).$$

(Hint: Begin with the expression for *s*(*T*,*p*) and use the definition of potential temperature.)

4. a. Explain why, for an ideal gas, the cyclic process shown below on a *p-V* diagram can only go counterclockwise or else it violates the Second Law of Thermodynamics.



b. **For some substances the process shown might be able to proceed clockwise. Explain why this might be possible.**