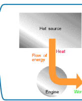
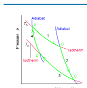
59-240 Lecture 10 Second Law Concepts

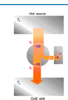
- **1st vs. 2nd law**
  - ΔU and ΔH
    - tell us what's thermodynamically permissible
    - do not tell us about spontaneity
    - Universe is a closed system
    - What drives processes forward?
- **Statements of the 2nd law**
  - Clausius — some work lost as heat
  - Lord Kelvin — some work lost as heat
  - Boltzmann — entropy does not decrease for an adiabatic system
  - Planck — perpetual motion machine of the second kind is impossible
  - Caratheodory — not all states can be reached via adiabatic processes
- **The Second Law**
  - Clausius/Kelvin
    - No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work

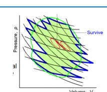
      - heat resevoir
      - cold sink
      - impossible engine
  - Processes
    - Bouncing ball
      - first law fulfilled
      - second law violated if ball bounces forever (perpetual motion machine of the 2nd kind)
    - Smashed egg
      - first and second laws fulfilled
      - reverse process never happens
    - Dispersal of energy
      - Some energy lost as random thermal energy (i.e., heat)
      - Spontaneous localization of motion is not possible
      - Boltzmann paradox
  - Entropy and Spontaneity
    - Energy must be dispersed
    - But, processes which increase order (decrease entropy) happen
    - Spontaneous/irreversible change - happens
    - Reversible change (not spontaneous, like equilibrium)
    - Impossible/highly improbable change (will not happen)
- **Entropy**
  - First Law: Permissible Changes via ΔU and ΔH
  - Second Law: Irreversible (Spontaneous) Changes via ΔS
  - $\Delta S_{total} > 0$
    - Note: same as ΔS_{univ}
    - $\Delta S_{total} = \Delta S_{sys} + \Delta S_{sur}$
  - Entropy, S
    - Measure of molecular-level disorder
    - Not a measure of macroscopic disorder (e.g., messy room)
  - Thermodynamic definition of S
    - $dS = \frac{dq_{rev}}{T}$ **infinitesimal change**
    - $\Delta S = \int_i^f \frac{dq_{rev}}{T}$ **measurable change**
    - Process along reversible path: S proportional to amount of heat produced/used
- **Clausius Inequality**
  - $dS_{sys} \geq \frac{dq}{T}$
  - all irreversible reactions are spontaneous and have a total entropy change which is greater than zero
  - isothermal expansion
    - reversible
      - $\Delta S_{sys} = q_{rev}/T = (0.693)nR$
      - $\Delta S_{sur,\,rev} = -(0.693)nR$
      - $\Delta S_{tot,\,rev} = 0$
    - irreversible
      - $\Delta S_{sys} = q_{rev}/T = (0.693)nR$
      - $\Delta S_{sur,\,irrev} = -(0.5)nR$
      - $\Delta S_{tot,\,irrev} = 0.193nR$
  - other processes
    - 1. irrev. adiabatic change — dq = 0, dS >= 0, dS_tot >=0
    - 2. Irrev. isothermal exp. of p.g. — dq = -dw, dS >=0, dS_sur=0, dS_tot >=0
    - 3. Spontaneous cooling
      - $dS = \frac{|dq|}{T_c} - \frac{|dq|}{T_h} = |dq|\left(\frac{1}{T_c} - \frac{1}{T_h}\right)$
      - dS > 0, dS_tot > 0 (unless Tc = Th)
- **Entropy as a State Function**
  - Cyclic process
    - $\oint \frac{dq_{rev}}{T} = 0$
  - Carnot Cycle

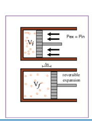
    - $\oint dS = \frac{q_h}{T_h} + \frac{q_c}{T_c}$ This is zero since: $\frac{q_h}{q_c} = -\frac{T_h}{T_c}$
    - ΔS = 0, proof
  - Efficiency
    - $\varepsilon = \frac{\text{work performed}}{\text{heat absorbed}} = \frac{|w|}{q_h}$
    - $\varepsilon_{rev} = 1 - \frac{T_c}{T_h}$

    - Cannot couple two eneinges together to increase efficiency
  - $\sum_{all} \frac{q_{rev}}{T} = \sum_{perimeter} \frac{q_{rev}}{T} = 0$

- **Surroundings**
  - Assumed not to change state when something happens to the system
  - $dS_{sur} = \frac{dq_{sur,\,rev}}{T_{sur}} = \frac{dq_{sur}}{T_{sur}}$
- **Entropy & Isothermal Expansion**

  - $p = p_{ex}$ | $\Delta T = 0$ | $\Delta V = V_f - V_i$, $w < 0$
  - $\Delta S = \frac{1}{T}\int_i^f dq_{rev} = \frac{q_{rev}}{T}$
  - $q_{rev} = -w_{rev} = nRT \ln\left(\frac{V_f}{V_i}\right)$
  - $\Delta S = nR \ln\left(\frac{V_f}{V_i}\right)$
  - Aside: $S = k \ln W$
    - Tendency to explore all available states