Laws of Thermodynamics

Thermodynamics

- Thermodynamics is the study of the effects of work, heat, and energy on a system
- Thermodynamics is only concerned with macroscopic (large-scale) changes and observations

Getting Started

- All of thermodynamics can be expressed in terms of four quantities
  - Temperature (T)
  - Internal Energy (U)
  - Entropy (S)
  - Heat (Q)
- These quantities will be defined as we progress through the lesson

Classical vs Statistical

- Classical thermodynamics concerns the relationships between bulk properties of matter. Nothing is examined at the atomic or molecular level.
- Statistical thermodynamics seeks to explain those bulk properties in terms of constituent atoms. The statistical part treats the aggregation of atoms, not the behavior of any individual atom

Introduction

According to British scientist C. P. Snow, the three laws of thermodynamics can be (*humorously*) summarized as

1. You can’t win
2. You can’t even break even
3. You can’t get out of the game

1.0 You can't win (1st law)

- The first law of thermodynamics is an extension of the law of conservation of energy
- The change in internal energy of a system is equal to the heat added to the system minus the work done by the system

$$\Delta U = Q - W$$

First Law of Thermodynamics

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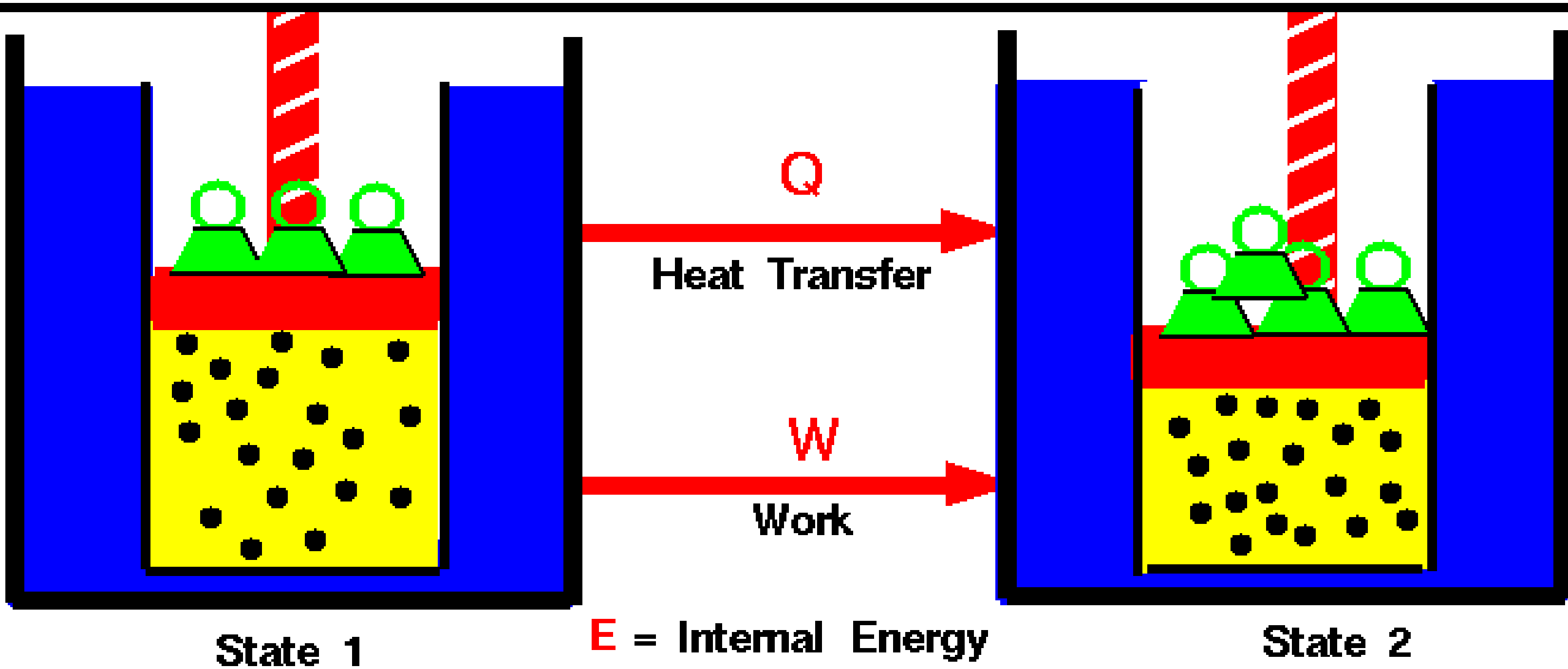

E = Internal Energy

$$E_2 - E_1 = Q - W$$

Any thermodynamic system in an equilibrium state possesses a state variable called the internal energy (E). Between any two equilibrium states, the change in internal energy is equal to the difference of the heat transfer into the system and work done by the system.

1.1 Process Terminology

- Adiabatic – no heat transferred
- Isothermal – constant temperature
- Isobaric – constant pressure
- Isochoric – constant volume

1.1.1 Adiabatic Process

- An adiabatic process transfers no heat
  - therefore $Q = 0$
- $\Delta U = Q - W$
- When a system expands adiabatically, W is positive (the system does work) so ΔU is negative.
- When a system compresses adiabatically, W is negative (work is done on the system) so ΔU is positive.

1.1.2 Isothermal Process

- An isothermal process is a constant temperature process. Any heat flow into or out of the system must be slow enough to maintain thermal equilibrium
- For ideal gases, if ΔT is zero, $\Delta U = 0$
- Therefore, $Q = W$
  - Any energy entering the system (Q) must leave as work (W)

1.1.3 Isobaric Process

- An isobaric process is a constant pressure process. ΔU, W, and Q are generally non-zero, but calculating the work done by an ideal gas is straightforward

$$W = P \cdot \Delta V$$

- Water boiling in a saucepan is an example of an isobar process

1.1.4 Isochoric Process

- An isochoric process is a constant volume process. When the volume of a system doesn’t change, it will do no work on its surroundings. $W = 0$

$$\Delta U = Q$$

- Heating gas in a closed container is an isochoric process

1.2 Heat Capacity

- The amount of heat required to raise a certain mass of a material by a certain temperature is called heat capacity

$$Q = mc_x\Delta T$$

- The constant c_x is called the specific heat of substance x, (SI units of J/kg·K)

1.2.1 Heat Capacity of Ideal Gas

- C_V = heat capacity at constant volume

$$C_V = 3/2\ R$$

- C_P = heat capacity at constant pressure

$$C_P = 5/2\ R$$

- For constant volume

$$Q = nC_V\Delta T = \Delta U$$

- The universal gas constant R = 8.314 J/mol·K

2.0 You can't break even (2nd Law)

- Think about what it means to not "break even". Every effort you put forth, no matter how efficient you are, will have a tiny bit of waste.
- The 2nd Law can also be stated that heat flows spontaneously from a hot object to a cold object (spontaneously means without the assistance of external work)

Second Law of Thermodynamics

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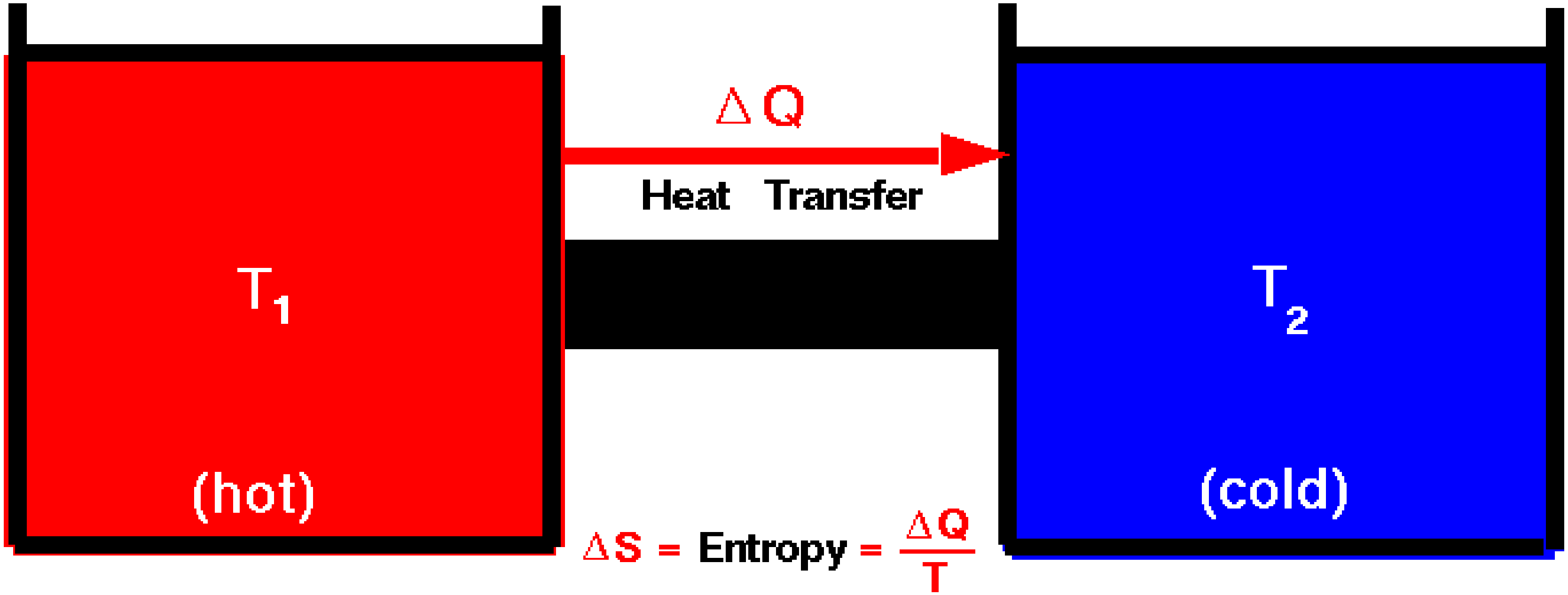


There exists a useful thermodynamic variable called entropy (S). A natural process that starts in one equilibrium state and ends in another will go in the direction that causes the entropy of the system plus the environment to increase for an irreversible process and to remain constant for a reversible process.

$S_f = S_i$ (reversible) $S_f > S_i$ (irreversible)

Slide courtesy of NASA

2.1 Concerning the 2nd Law

- The second law of thermodynamics introduces the notion of entropy (S), a measure of system disorder (messiness)
- U is the quantity of a system's energy, S is the quality of a system's energy.
- Another C.P. Snow expression:
  - not knowing the 2nd law of thermodynamics is the cultural equivalent to never having read Shakespeare

2.2 Implications of the 2nd Law

- Time marches on
  - If you watch a movie, how do you know that you are seeing events in the order they occurred?
  - If I drop a raw egg on the floor, it becomes extremely “disordered” (greater Entropy) – playing the movie in reverse would show pieces coming together to form a whole egg (decreasing Entropy) – highly unlikely!

2.3 Direction of a Process

- The 2nd Law helps determine the preferred direction of a process
- A reversible process is one which can change state and then return to the original state
- This is an idealized condition – all real processes are irreversible

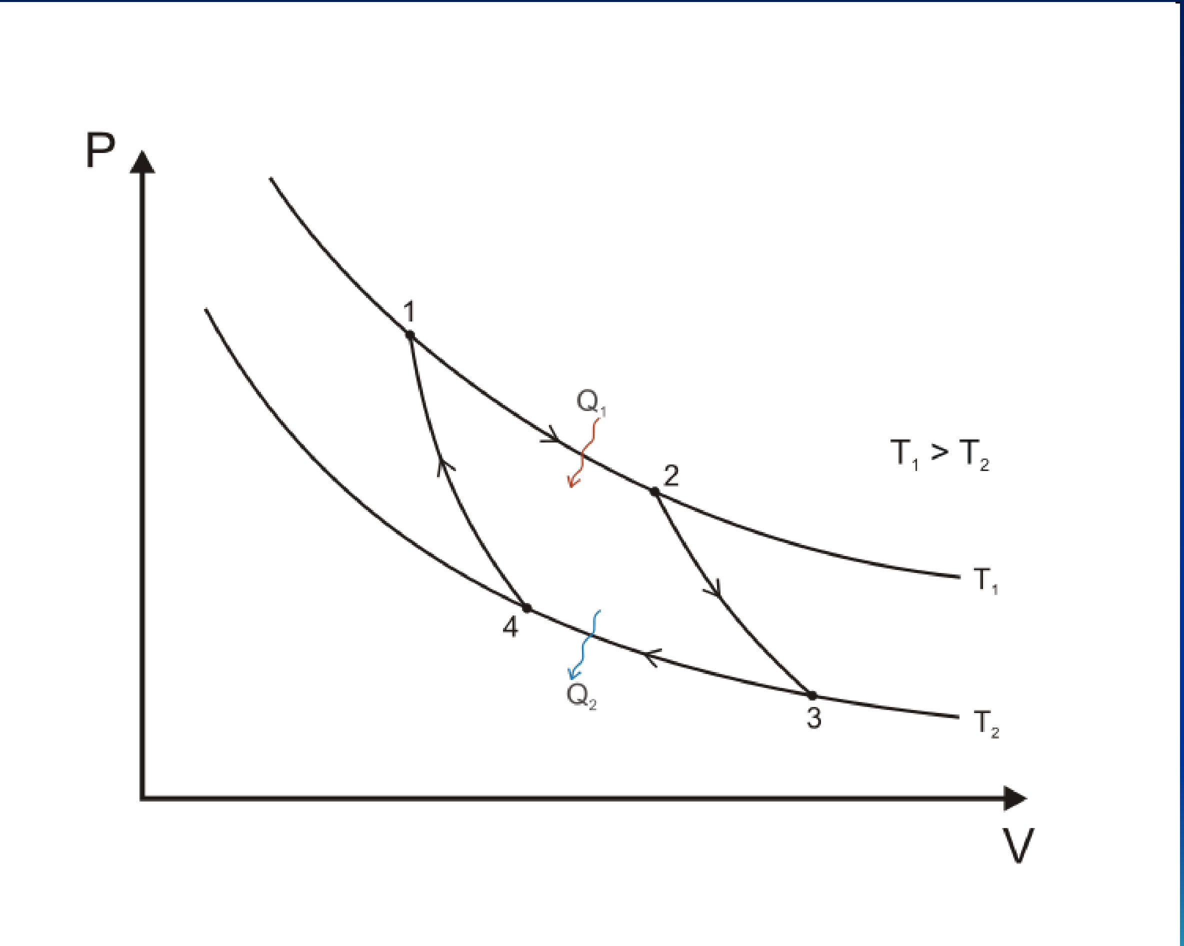
2.4 Heat Engine

- A device which transforms heat into work is called a heat engine
- This happens in a cyclic process
- Heat engines require a hot reservoir to supply energy (Q_H) and a cold reservoir to take in the excess energy (Q_C)
  - Q_H is defined as positive, Q_C is negative

2.4.1 Cycles

- It is beyond the scope of this presentation, but here would be a good place to elaborate on:
  - Otto Cycle
  - Diesel Cycle
  - Carnot Cycle
    - Avoid all irreversible processes while adhering to the 2nd Law (isothermal and adiabatic only)

2.4.2 The Carnot Cycle



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2.4.2.1 Carnot explained

- Curve A ($1 \rightarrow 2$): Isothermal expansion at T_H
  - Work done *by* the gas
- Curve B ($2 \rightarrow 3$): Adiabatic expansion
  - Work done *by* the gas
- Curve C ($3 \rightarrow 4$): Isothermal compression at T_C
  - Work done *on* the gas
- Curve D ($4 \rightarrow 1$): Adiabatic compression
  - Work done *on* the gas

2.4.2.2 Area under PV curve

- The area under the PV curve represents the quantity of work done in a cycle
- When the curve goes right to left, the work is negative
- The area enclosed by the four curves represents the net work done by the engine in one cycle

2.5 Engine Efficiency

- The thermal efficiency of a heat engine is

$$e = 1 + Q_C/Q_H$$

- The “engine” statement of the 2nd Law:
  - it is impossible for any system to have an efficiency of 100% (e = 1) [Kelvin’s statement]
- Another statement of the 2nd Law:
  - It is impossible for any process to have as its sole result the transfer of heat from a cooler object to a warmer object [Clausius’s statement]

2.6 Practical Uses

- Automobile engines, refrigerators, and air conditioners all work on the principles laid out by the 2nd Law of Thermodynamics
- Ever wonder why you can’t cool your kitchen in the hot summer by leaving the refrigerator door open?
  - Feel the air coming off the back - you heat the air outside to cool the air inside
  - See, you can’t break even!

3.0 You can't get out (3rd Law)

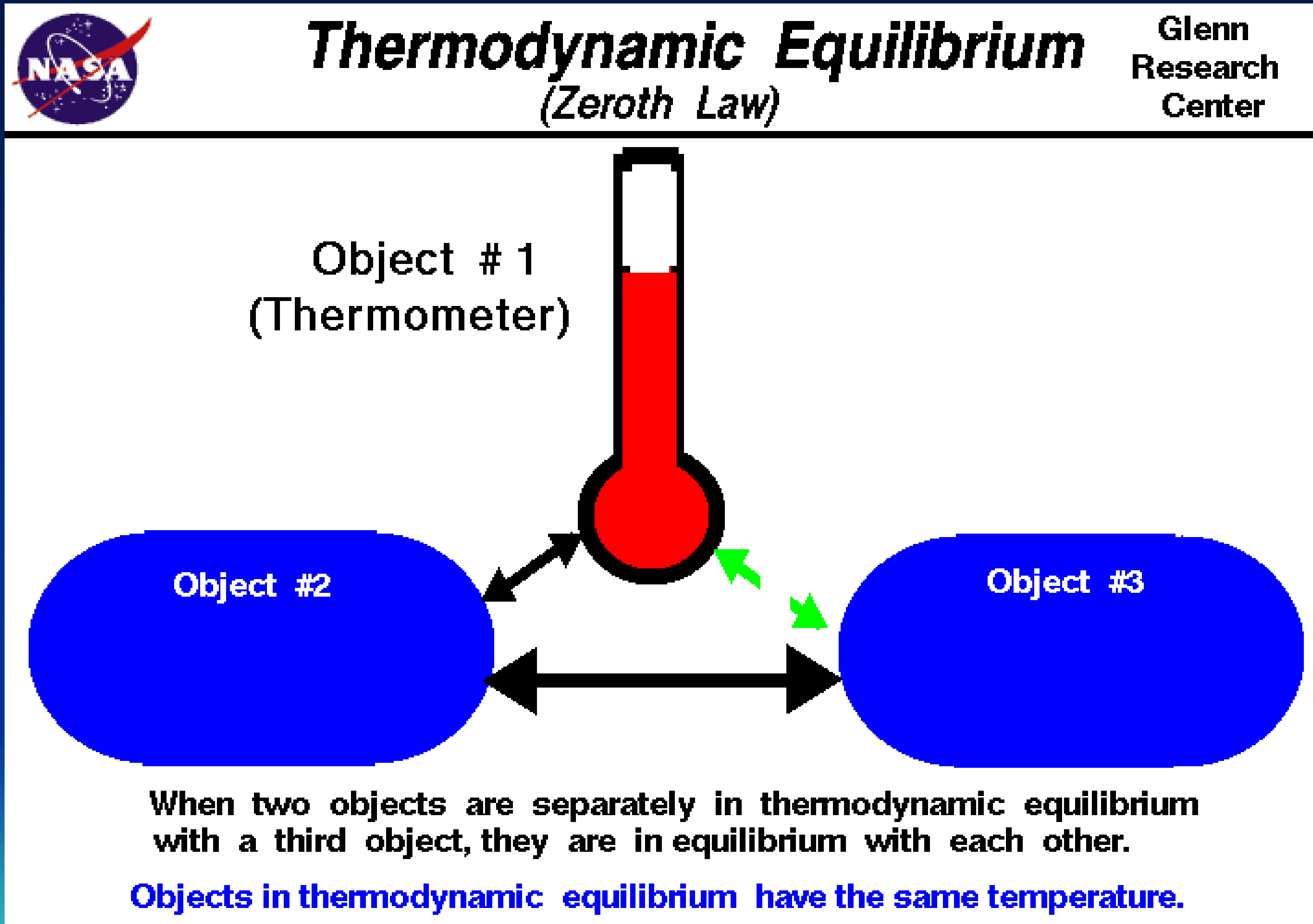
- No system can reach absolute zero
- This is one reason we use the Kelvin temperature scale. Not only is the internal energy proportional to temperature, but you never have to worry about dividing by zero in an equation!
- There is no formula associated with the 3rd Law of Thermodynamics

3.1 Implications of 3rd Law

- MIT researchers achieved 450 picokelvin in 2003 (less than ½ of one billionth!)
- Molecules near these temperatures have been called the fifth state of matter: *Bose-Einstein Condensates*
  - Awesome things like super-fluidity and super-conductivity happen at these temperatures
  - Exciting frontier of research

4.0 The Zeroth Law

- The First and Second Laws were well entrenched when an additional Law was recognized (couldn't renumber the 1st and 2nd Laws)
- If objects A and B are each in thermal equilibrium with object C, then A and B are in thermal equilibrium with each other
- Allows us to define temperature relative to an established standard



Slide courtesy of NASA

4.1 Temperature Standards

- See Heat versus Temperature slides for a discussion of these two concepts, and the misconceptions surrounding them
  - Heat is energy transfer
  - Temperature is proportional to internal energy
  - Fahrenheit, Celsius, and Kelvin temp scales