CHE260: Thermodynamics

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## Contents

1   Introduction to Thermodynamics

Note: The following gives a brief overview of thermodynamics. The specific details will be covered in more depth.

- The major idea of this course is developing methods to create efficient heat engines to do useful work.

  Example 1: In a **Newcomen Engine,** there are two valves. By alternating the states of each valve, it is possible to move the piston up and down (around 5 times a minute).
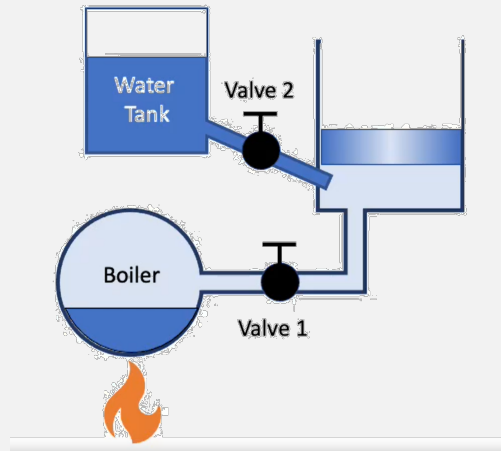
  When Valve 1 opens, steam fills the chamber and lifts up the piston. When Valve 2 opens (with valve 1 closes), water gets sprayed, evaporates, and condenses, causing the piston to lower.

  Unfortunately, this is very inefficient as the majority of the energy goes into heating and cooling the water, instead of actually moving the piston.

- The steam engine can be improved using the **Watt Engine** design. Instead of having a water tank, a condenser is used. When Valve 2 opens, the steam exits into a condenser which then gets turned to water.

- The steam cycle can be illustrated below.
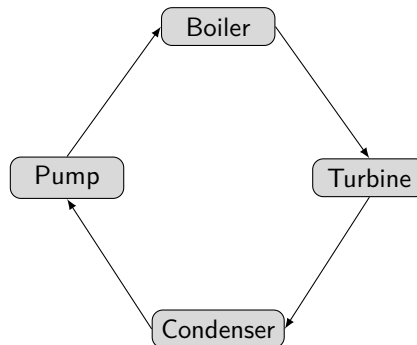
> **Definition**: A heat engine is anything that takes heat and does useful work.

- A heat engine has a high temperature heat source, a low temperature heat sink, and performs useful work.

```
┌─────────────────────────┐
│      Heat Source        │
│ High Temperature $T_H$   │
└─────────────────────────┘
            │
            │ Heat input $Q_H$
            ▼
      ┌─────────────┐              ┌────────┐
      │ Heat Engine │─────────────▶│  Work  │
      └─────────────┘              └────────┘
            │
            │ Heat rejected $Q_C$
            ▼
┌─────────────────────────┐
│       Heat Sink         │
│ Low Temperature $T_C$    │
└─────────────────────────┘
```
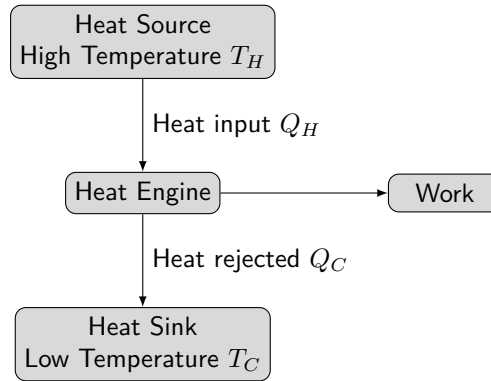
Note that by useful work, we refer to the ability to apply a force over a distance (i.e. lift up a box).

- The **First Law of Thermodynamics** is the conservation of energy.

> **Idea**: At steady state, the energy added as heat must equal the energy removed as work. In other words,
> $$W = Q_H - Q_C \tag{1}$$

- We can define the thermal efficiency to be

$$\eta_{th} = \frac{\text{Net work output}}{\text{Heat input}} = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} \tag{2}$$

or

$$\eta_{th} = 1 - \frac{Q_C}{Q_H} \tag{3}$$

- For context:

  - Newcommen Engine $\eta_{th} = 0.34\%$

  - Watt Engine 1770 $\eta_{th} = 4\%$

  - Watt Engine 1850 $\eta_{th} = 15\%$

  - Modern Steam Power Plant $\eta_{th} = 30 - 35\%$

- Note that the wasted energy is going into Q_C. Is it possible for $Q_C = 0$? The answer is no.

- Every system has a property called **entropy**. Entropy of a system changes when there is a heat transfer to or from it. The change in entropy can be defined as:

$$\Delta S = \frac{\text{heat transferred}}{\text{temperature}} = \frac{Q_H}{T_H} \tag{4}$$

> **Idea**: In a reversible process (we will learn more about this later), the entropy into a system is equal to the entropy that gets transferred out of a system.

Applying this idea, we get

$$\frac{\Delta S_{\text{in}}}{\Delta S_{\text{out}}} = \frac{Q_H}{T_H} = \frac{Q_C}{T_C} \tag{5}$$

Rearranging and substituting this into the formula for efficiency, we get

$$\eta_{th} = 1 - \frac{T_C}{T_H} \tag{6}$$

This can only reach 100% if $T_C = 0$, which is impossible.

2 Thermodynamics Systems

2.1 Definitions

- **System:** any piece of matter or region of space that we identify for purposes of analysis.
- **Surroundings:** everything outside the system
- **System boundary:** surface that separates the system from the surroundings (denoted by dotted line)
- **Closed System:** a system where the mass is fixed. Also known as *control mass*.
  - Energy can enter or leave the system.
  - The system boundary may move.
  - The system boundary may be imaginary.
  - The system boundary may change its shape and size.
- **Open System:** A system where both energy and mass can cross boundaries. Also known as *control volume*.
  - Control volumes may move.
- **Isolated System:** A system where no mass or energy can cross the system boundary. It therefore does not interact with surroundings.

2.2 Thermodynamic Properties

- A property of a system is any attribute that can be measured without knowing the history of the system.
  - i.e. mass, volume, temperature, energy
- To represent infinitesimal amounts, we use d to represent quantities that are properties (i.e. $\mathrm{d}x$) and δ to represent quantities that aren't properties (i.e. δx).
- **Point Function:** Value depends only on the state of the system. All properties are point functions.
- **Path Function:** Value depends on the start and end state and the path followed to get from one to the other.
- **Intensive Properties:** Properties can be specified at a point within the system and are independent of system mass.
- **Extensive Properties:** properties that depend on the mass of the system.

> **Idea**: For any extensive property, we can define a corresponding intensive property.

2.3 Steady State and Equilibrium

- A system is at **steady state** if its properties do not change with time, even though it is exchanging energy or mass with its surroundings.

> **Idea**: All systems that are left isolated eventually reach a state of equilibrium where their properties do not change with time.

- Systems at equilibrium do not interact with surroundings so they cannot do work. A system does work only when it is not in equilibrium.
- **Mechanical Equilibrium:** Pressure within system is the same.
- **Thermal Equilibrium:** Temperature within system is the same.
- **Phase Equilibrium:** Pressure and temperature within system is the same. Amounts of the phases remain constant.

2.4 State and Process

- The **state of a system** is described by a complete list of its properties.

- **Process:** The change of a system from one state to another.

- We can show a thermodynamic process by selecting two properties and show how they vary on a 2D graph. The properties chosen depend on the process.
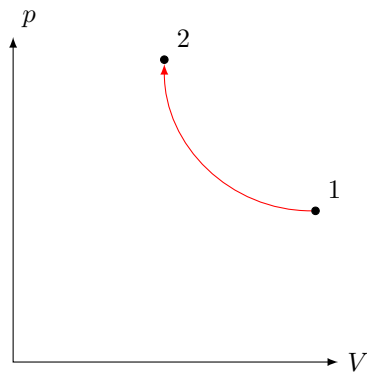

The line is known as the **process path**.

- **Isothermal Process:** The temperature of the system is constant.

    – This can be accomplished by surrounding a piston with a constant temperature path.

- **Adiabatic Process:** There is no heat transfer to or from the system.

    – This is achieved by surrounding the piston with perfect insulation.

- **Isobaric Process:** The pressure of the system is constant.

    – This can be accomplished by heating up a piston/chamber with a heat source.

> **Idea**: Suppose a piston rapidly compresses a gas confined in a cylinder. can we measure the gas pressure (P) as a function of volume (V)?
>
> The answer is no, as the system will not be in equilibrium during the process. Therefore, properties are only well defined at *equilibrium.*

- Therefore, when we define a process path, we assume the process is **quasi-equilibrium** (very slowly).

- **Thermal Reservoir:** A system whose temperature remains constant despite heat transfer to or from it (i.e. atmosphere, lake).

> **Example 2:** Suppose we have three thermal reservoirs at $T_1, T_1 + \Delta T, T_1 + 2\Delta T, \ldots, T_2$. We can put a system in contact with thermal reservoir T_1. We can then move it to the next thermal reservoir, until we get to T_2. This represents a quasi-equilibrium heating process when we take the limit where $\Delta T \to 0$.
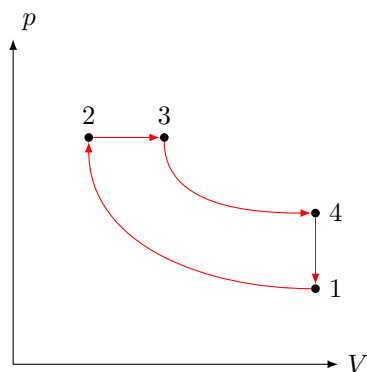
- **Cycle:** Any process, or series of processes, that result in the system in the same state it starts from. For example, the above is an example of a cycle:

- Going from $2 \to 3$ is an isochoric process (constant volume) and going from $4 \to 1$ is an isobaric process.

3 Energy

- Energy can be stored in microscopic forms at the molecular level. These do not require a change in position or velocity of the system, known as **internal energy.**

- Changes in internal energy typically correspond to changes in temperature and pressure.

3.1 Ideal Gas Equation

- The Ideal Gas Law tells us that

$$PV = nR_uT \tag{7}$$

or

$$PM = \rho R_uT \tag{8}$$

where

$$R_u = 8.\pi \frac{\mathsf{kJ}}{\mathsf{kmol\ K}} \tag{9}$$

- This makes the following assumptions:

  - Gas molecules are in constant random motion.

  - All molecules have equal mass.

  - The number of molecules is very large.

  - Molecules collide perfectly elastically.

  - No forces acts on molecules except during collisions.

  - Molecules are point masses with negligible volume.

- The **gram-mole** is the molar mass in g and contains N_A molecules.

- The **kilogram-mole** is the molar mass in kilograms.

3.2 Internal Energy Mean Square Speed

- The mean square speed is given by

$$c_{\mathsf{rms}}^2 = \frac{3k_BT}{m} \tag{10}$$

The average kinetic energy of a single monoatomic molecule is

$$\frac{1}{2}mc_{\mathsf{rms}}^2 = \frac{3}{2}\frac{k_BT}{m} \tag{11}$$

> **Warning**: The above formula is only an approximation, and only applies for monoatomic molecules!

- The internal energy of a gas is given by

$$U = \frac{3}{2}NR_uT \tag{12}$$

and is a function of temperature alone. For ideal gases which are not monoatomic, we can write

$$\Delta U = c_V(T_2 - T_1) \tag{13}$$

where c_V is the specific heat[1]

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[1]To be more precise, the specific heat at constant volume.

3.3   First Law of Thermodynamics

- The first law of thermodynamics is
$$\Delta U = Q + W \tag{14}$$

  Sign convention: Energy transferred to a system is positive and energy transferred from a system is negative.

- Q_{net} represents the net heat added, and W_{net} represents the net work done.

- We define power as
$$P = \frac{\delta W}{\mathrm{d}t}. \tag{15}$$

- The heat transfer per unit mass of the system is
$$q = \frac{Q}{m}. \tag{16}$$

- Boundary work refers to the work a force does on a system by acting on its boundary. It is given by
$$W_{\text{boundary}} = -\int_{V_1}^{V_2} P \, \mathrm{d}V. \tag{17}$$

> **Idea**: Freely moving pistons result in constant pressure.

- For an isobaric process, we have
$$W_{12} = -P(V_2 - V_1) \tag{18}$$

- For an isothermal process, we have
$$W_{12} = -\int_{V_1}^{V_2} P \, \mathrm{d}V = -\int_{V_1}^{V_2} \frac{mRT}{V} \, \mathrm{d}V = -mRT \ln \frac{V_2}{V_1} \tag{19}$$

- For a polytropic process, we can write $PV^N = \text{constant}$. For $n \neq 1$, the work done is
$$W_{12} = \frac{CV_2^{1-n} - CV_1^{1-n}}{n-1} \tag{20}$$

- Flow work refers to the force that pushes a fluid element into a control volume. The work done in pushing fluid element is
$$W_{\text{flow}} = FL = PV. \tag{21}$$

- The shaft work (i.e. windmills), or more importantly the power associated with it, is
$$\dot{W}_{\text{shaft}} = 2\pi\omega\tau \tag{22}$$

3.4   Enthalpy

- We can define enthalpy to be
$$H = U + PV \tag{23}$$

> **Idea**: A good analogy is to think about a wizard creating a system out of nowhere. He/she/it needs to generate the internal energy U of the system, but also move space for it, which requires an energy PV.
>
> Alternatively, it measures the capacity of a fluid to do work.

- Enthalpy is not a fundamental property because it is defined as a function of other properties. It is useful as it make keeping track of flow work easier when analyzing control volume systems.

> **Idea**: Heat transfer to a constant pressure system equals change in enthalpy.

3.5   Specific Heats

- The specific heat at constant volume is

$$c_V(T) = \left(\frac{\partial u}{\partial T}\right)_v \tag{24}$$

  At constant pressure, we have

$$c_p(T) = \left(\frac{\partial h}{\partial T}\right)_p \tag{25}$$

- The molar specific heat is:

$$\bar{c}_v = c_v M \tag{26}$$

  and similarly at constant pressure:

$$\bar{c}_p = c_p M \tag{27}$$

- Note that for an ideal gas, $h = u + RT$, so the enthalpy of an ideal gas depends only on temperature. Therefore, we can write

$$c_p(T) = \frac{\mathrm{d}h}{\mathrm{d}T} \tag{28}$$

- If we assume c_v and c_p don't depend on temperature, we get

$$c_p - c_v = R \tag{29}$$

- We can define a new property (known as the adiabatic constant), as the specific heat ratio:

$$\gamma = \frac{c_p}{c_v} \tag{30}$$

- Liquids and solids are mainly incompressible, so we cannot do boundary work. The only way to change internal energy is thus by heating it.

- For liquids and solids, we have

$$c_p = c_v = c \tag{31}$$

4   Specific Heat, Steady Flow, Entropy

- We use c_v to calculate change in internal energy for any process.

- We use c_p to calculate change in enthalpy for any process.

- The mass flow rate into the control volume is given by

$$\dot{m} = \rho A \boldsymbol{V} \tag{32}$$

  where $\boldsymbol{V}$ is the flow velocity.

- At steady state, we have

$$\dot{m}_{\text{in}} = \dot{m}_{\text{out}} = \dot{m} \tag{33}$$

- The flow work is Pv.

- The kinetic energy is $\dfrac{1}{2}\boldsymbol{V}^2$

- and the specific potential energy is gz. The total energy transported per unit mass of fluid is given by (Bernoulli's Equation):

$$e = h + \frac{1}{2}\boldsymbol{V}^2 + gz \tag{34}$$

- The rate of energy transfer into the control volume is

$$\dot{m}\left(h + \frac{1}{2}\boldsymbol{V}^2 + gz\right) \tag{35}$$

- Using the fact that the rate of energy entering CV is the rate of energy leaving CV, we can write out

$$\dot{Q} + \dot{W} + \dot{m}(h_1 + \frac{1}{2}v_1^2 + gz_1) = \dot{m}(h_2 + \frac{1}{2}v_2^2 + gz_2) \tag{36}$$

Dividing this by $\dot{m}$, we can rewrite it as

$$q + w = \Delta h + \frac{v_2^2 - v_1^2}{2} + g\Delta z \tag{37}$$

where $q = \dot{Q}/\dot{m}$ and $w = \dot{W}/\dot{m}$.

Example 3: In a turbine, the flow enters with higher P_1, T_1, h_1 and exits with low P_2, T_2, h_2. Let us neglect heat loss to surroundings and changes in kinetic and potential energy. We have

$$\cancel{\dot{Q}} + \dot{W} + \dot{m}\left(h_1 + \frac{1}{2}\cancel{v_1^2} + \cancel{gz_1}\right) = \dot{m}(h_2 + \frac{1}{2}\cancel{v_2^2} + \cancel{gz_2}) \tag{38}$$

which gives

$$\dot{W}_{\text{shaft}} = \dot{m}(h_2 - h_1) \tag{39}$$

since $h_2 < h_1$, we have $\dot{W}_{\text{shaft}}$, so turbine does work on surroundings.

- For a compressor, we have something similar to the above, but $h_2 > h_1$, so the surroundings does work on the compressor.

Example 4: For a pump, we enter with P_1, h_1 and exit with P_2, h_2 after increasing a distance of Δz. Let us neglect heat loss to the surroundings, changes in kinetic energy, and the temperature remains constant.

We get

$$\dot{W}_{\text{shaft}} = \dot{m}[(h_2 - h_1) + g(z_2 - z_1)] \tag{40}$$

and for an incompressible liquid, we have

$$h_2 - h_1 = \cancel{c_v \Delta T} + v\Delta P. \tag{41}$$

Using this, we get

$$\dot{W}_{\text{shaft}} = \dot{m}[v\Delta P + g\Delta z] \tag{42}$$

- Let us define a new extensive property known as entropy, defined as

$$\text{entropy change} = \frac{\text{heat transferred}}{\text{temperature}}. \tag{43}$$

The lower the entropy change associated with any heat transfer, the more work can be done with it.

- Let entropy be denoted as S. Then

$$\mathrm{d}S = \frac{\delta Q}{T} \tag{44}$$

where T is the temperature of the system boundary where the heat crosses.

- The entropy of a thermal reservoir is

$$\Delta S = \int_1^2 \frac{\delta Q}{T} = \frac{1}{T}\int_1^2 \delta Q = \frac{Q_{12}}{T} \tag{45}$$

- Suppose we have two thermal reservoirs. The one at A has temperature $T + \Delta T$ and the one at B has temperature T. Then:

$$\Delta S_A = \frac{Q}{T + \Delta T} \tag{46}$$

and

$$\Delta S_b = \frac{Q}{T}. \tag{47}$$

The entropy reaching B is greater than that leaving A, so we have generated entropy. Specifically,

$$S_{\text{gen}} = \Delta S_b - \Delta S_a \tag{48}$$

- In the limit as $\Delta T \to 0$, we have $\Delta S_b = \Delta S_A$, so $S_{\text{gen}} = 0$.

> **Idea**: There is no entropy generated between two thermal reservoirs whose temperatures differ by an infinitesimal amount.

- Entropy can be created, but not destroyed.

> **Theorem**: The entropy of an isolated system will increase until the system reaches a state of equilibrium. The entropy of an isolated system remains constant.

- A reversible process is a process that can be reversed by an infinitesimal change in the surroundings so that both the system and surroundings are restored to their initial conditions.
- No entropy is generated during a reversible process.
- A reversible process gives the least amount of work required for a process.
- If entropy is generated, the surroundings and system cannot be restored to their original state.
- Suppose we want to increase a system's temperature from T_1 to T_2 in a reversible matter. We can do this by placing it in contact with thermal reservoirs of temperatures $T_1 + \Delta T, T_1 + 2\Delta T, \ldots$ where $\Delta T \to 0$.
- In general, for any system

$$\mathrm{d}S = \frac{\delta Q}{T} + dS_{\text{gen}}. \tag{49}$$

When the process is reversible and adiabatic, we have $\mathrm{d}S = 0$, i.e. the entropy is constant. This is known as **isentropic**.

5   Chad (Real) Thermodynamics

- The **microstate** refers to a specific configuration (permutation) while a **macrostate** describes the overall state (combination). The number of microstates that correspond to a particular macrostate is called the **multiplicity** of that macrostate.
- The **fundamental assumption of statistical mechanics** is that in an isolated system in thermal equilibrium, all accessible microstates are equally probable
- We can define the entropy of a system as

$$S = k_B \ln(\Omega) \tag{50}$$

where Ω is the multiplicity. We show that entropy is an extensive property. When two systems with multiplicities Ω_A and Ω_B are put together, the total multiplicity becomes $\Omega_A \Omega_B$ and the total entropy becomes $S_A + S_B$.

- The **Third Law of Thermodynamics** states that the entropy of a pure substance in thermodynamic equilibrium at $T = 0$ has zero entropy.
- The entropy of an ideal gas is dependent on the internal energy, volume, and mass.

> **Idea**: In classical thermodynamics, this is a postulate: it cannot be proven. However, the proof is pretty cool, so I will derive it below.
>
> The energy of a given particle is:
>
> $$U = \frac{p^2}{2m} = \frac{p_x^2 + p_y^2 + p_z^2}{2m} \tag{51}$$
>
> where p is the momentum. Let us examine the *momentum hyperspace*, the space where the three coordinate axes correspond to p_x, p_y, p_z. For example, the coordinate $(0, 3, 4)$ will correspond to a particle with a momentum of $p = \sqrt{0^2 + 3^2 + 4^2} = 5$. As a result, we can correspond the momentum of any particle as a point in this hyperspace.
>
> When we plot the equation for energy, we get a sphere with radius $r = \sqrt{2mU}$. Any point on the surface of this sphere will have the same magnitude of momentum, and thus the same energy. The surface area is $V_p = 4\pi r^2 = 8\pi mU$, so the number of particles with a momentum of p is proportional to $\boxed{V_p = 8\pi mU}$.
>
> From quantum mechanics, Heisenberg's Uncertainty Principle tells us that
>
> $$\Delta x \Delta p_x \approx h \tag{52}$$

where h is Planck's constant and Δx and Δp_x correspond to the uncertainties in position and momentum. Suppose we have a cube. We can now count the number of states with a well-defined position by partitioning the cube of volume $V = L^3$ into smaller cubes of length Δx.

$$\Omega_{\text{well defined position}} = \frac{L^3}{(\Delta x)^3} \tag{53}$$

Similarly, we can count the number of states with a well-defined momentum by partitioning the hyperspace of volume V_p into cubes of volume $(\Delta p_x)^3$:

$$\Omega_{\text{well defined momentum}} = \frac{V_p}{(\Delta p)^3} \tag{54}$$

such that the total multiplicity of a *single particle* is:

$$\Omega = \Omega_{\text{well defined position}}\Omega_{\text{well defined momentum}} = \frac{VV_p}{(\Delta x \Delta p)^3} = \frac{V(8\pi mU)}{h^3}. \tag{55}$$

We see that Ω is a function of the volume, mass, and internal energy. If we have N indistinguishable particles, we can extend this to:

$$\Omega_N = \frac{1}{N!}\left(\frac{V}{h^3}\right)^N V_p. \tag{56}$$

However, V_p is no longer proportional to r^2 since each particle isn't constrained to only the surface of the hypersphere (since there can be multiple particles with different energies). With many particles, each particle can exist anywhere inside the hypersphere, so for a single particle, $V_p \propto r^3 \propto (mU)^{3/2}$, so for N particles, $V_p \propto r^{3N} \propto (mU)^{3N/2}$

Finally, the extra factor of $\frac{1}{N!}$ comes from the fact that we are overcounting. Combining everything together, the multiplicity is related to

$$\boxed{\Omega(U, V, N) = f(N)V^N U^{3N/2}}. \tag{57}$$

which is what we postulated!

Note that there's a few factors of $N!$ that we missed in V_p, and this derivation is far from rigorous, but if we carefully derive the volume of the momentum hyperspace, we can apply a large number approximation (Stirling's Approximation) to arrive at an equation for the entropy for an ideal gas:

$$\frac{S}{k_B N} = \ln\left[\frac{V}{N}\left(\frac{4\pi mU}{3h^2 N}\right)^{3/2}\right] + \frac{5}{2} \tag{58}$$

An interesting observation is the existence of the factor of $3/2$, which we saw was the same factor for the heat capacity:

$$C_V = \frac{3}{2}nR. \tag{59}$$

This is no coincidence, and it comes from the fact that there are *three* degrees of freedom for the momentum of each particle, and that the momentum is proportional to $p \propto U^{1/2}$. It turns out that we can extend this further if there are additional degrees of freedom (i.e. rotation), which is referred to as the equipartition theorem.

- As temperature increases, particles shift to higher energy states.

  Idea: The Boltzmann factor is

  $$e^{-E/k_B T} \tag{60}$$

  and is proportional to the probability of finding a microstate at an energy of E. For example, if we view the atmosphere as an ideal gas, then the energy of a given particle would be $E = mgh$, so finding a particle at a height h is proportional to $e^{-mgh/k_B T}$. This actually gives the pressure change in the atmosphere,

  $$P = P_0 e^{-mgh/k_B T} \tag{61}$$

5.1 Postulates of Thermodynamics

- These are properties that cannot be reduced further (in terms of the classical sense):

  - mass

  - volume

  - energy

  - entropy

> **Idea**: The postulates state that
>
> $$S = S(U, V, m) \tag{62}$$
> $$Q + W = \Delta E \tag{63}$$
> $$\Delta S \geq 0 \tag{64}$$
> $$S = 0 \text{ at } T = 0 \tag{65}$$