PHYS-2010: General Physics I
Course Lecture Notes
Section XIV

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Abstract

These class notes are designed for use of the instructor and students of the course PHYS-2010: General Physics I taught by Dr. Donald Luttermoser at East Tennessee State University. These notes make reference to the *College Physics, 11th Edition* (2018) textbook by Serway and Vuille.

XIV.   Thermodynamics

A. The area of physics concerned with the relationships between heat and work is **thermodynamics** $\Longrightarrow$ the study of the motion of heat.

B. The First Law of Thermodynamics.

1. In words: **The change in internal energy of a system equals the difference between the heat taken in by the system and the work done on the system.**

   a) When an amount of heat Q is added to a system, some of this added energy remains in the system increasing its internal energy by an amount ΔU.

   b) The rest of the added energy leaves the system as the system does work W.

2. Mathematically, note that

$$\Delta U = U_\mathrm{f} - U_\mathrm{i} \ ,$$

   and the First Law states

$$\boxed{\Delta U = Q + W \ .} \qquad\qquad \text{(XIV-1)}$$

3. In thermodynamics, there will always be two specific regions in which we will be interested in:

   a) The **system** — the region of interest where we wish to know the state parameters (*e.g.*, P, T, and V). Thermodynamic variables relating to the system will remain 'unsubscripted' in these notes (*i.e.*, $W =$ work on the system).

b) The **environment** (also called the *universe*) — the region that contains the system. Note that some scientists (including me) prefer to use the word *environment* over *universe* since in astronomy the word **Universe** means all of the cosmos and <u>not</u> just the immediate (*i.e.*, nearby) surroundings which is what thermodynamics means by "universe." Thermodynamic variables relating to the environment will be labeled with the 'env' subscript in these notes (*i.e.*, W_{env} = work on the environment).

c) Note that work done <u>on</u> the <u>system</u> W is the exact opposite of work done <u>on</u> the <u>environment</u>:

$$W = -W_{\text{env}} \ .$$

4. We will often be interested in systems that are completely isolated from the environment. Such a system is called a **closed system**.

5. Using the definition of work (Eq. VI-1) and pressure (Eq. XI-1), we can show how work is related to the change in volume of gas.

a) Work will increase in small increments ΔW as a piston in a cylinder moves by a length Δx, then

$$\Delta W = -F\,\Delta x = -\frac{F}{A}\,(\Delta x \cdot A) = -P\,\Delta V \ , \quad \text{(XIV-2)}$$

note that the negative sign in this relation results from the fact that when the environment does work <u>on</u> the cylinder (*i.e.*, the system), ΔV becomes smaller (hence $\Delta V < 0$) due to the piston's motion. As such, the work done on the system is positive ($W > 0$). Since Δx is a very small length in this equation, P will not change by much. As such, P is considered to be constant in this equation.

b) The total work done W is then just the sum of all of the incremental increases in work:

$$W = \sum_i \Delta W_i = -\sum_i P_i \, \Delta V_i \; . \qquad \text{(XIV-3)}$$

However, the shorthand notation of

$$W = -P\Delta V \qquad \text{(XIV-4)}$$

is often used for Eq. (XIV-3) and we will use this notation here.

c) A gas-filled cylinder with a piston is the simplest form of a **heat engine**. Such heat engines are used to drive more complicated machines such as automobiles.

6. For a monatomic ideal gas (*i.e.*, the gas particles consist of a single atomic species), recall Eq. (XIII-17) where the internal energy is given by

$$U = \frac{3}{2}nRT \; .$$

a) The change in internal energy for such a gas is then given by

$$\Delta U = \frac{3}{2}nR\Delta T \qquad \text{(XIV-5)}$$

(assuming no gas escapes or is brought into the system).

b) We will now introduce a new thermodynamic term call the **molar specific heat at constant volume** for a monatomic ideal gas:

$$C_v \equiv \frac{3}{2}R \; . \qquad \text{(XIV-6)}$$

c) The change in internal energy of an ideal gas can then be written as

$$\Delta U = nC_v\Delta T \; . \qquad \text{(XIV-7)}$$

d) For ideal gases, this expression is <u>always</u> valid, even when the volume isn't constant. The value of the molar specific heat, however, depends on the gas (*e.g.*, the numbers of *degrees of freedom* the gas can have) and can vary under different conditions of temperature and pressure.

7. There are four specific types of processes involving energy in thermodynamics:

a) **Isobaric processes**: Pressure remains constant during the process. The full form of the 1st law is used in these cases.

i) Under these conditions, the thermal energy transferred into the gas (*i.e.*, system) is given by rearranging the terms in the first law:

$$Q = \Delta U - W = \Delta U + P\Delta V \ ,$$

where here we have made use of Eq. (XIV-4) in this relation.

ii) Using Eq. (XIV-5) and Form 1 of the ideal gas law (*i.e.*, $P\Delta V = nR\Delta T$) in this relation gives

$$Q = \frac{3}{2}nR\Delta T + nR\Delta T = \frac{5}{2}nR\Delta T \ .$$

iii) Another way to express this transfer of heat is

$$Q = nC_p\Delta T \ , \qquad\qquad \text{(XIV-8)}$$

where $C_p = \frac{5}{2}R$ is the **molar specific heat at constant pressure**.

iv) For ideal gases, the molar heat capacity at constant pressure is equal to the sum of the molar specific heat at constant volume and the universal gas

constant:

$$C_p = C_v + R \ . \qquad \text{(XIV-9)}$$

b) **Adiabatic processes**: Heat does not enter or leave the system — only occurs for closed systems or *effectively* closed systems. A good example of an adiabatic process is anything that happens so rapidly that heat does not have time to flow in or out of the system during the process. Then $Q = 0$ and Eq. (XIV-1) becomes

$$\Delta U = W \qquad \text{(adiabatic processes)}.$$

i) If the system does work on the environment, $W < 0$ (negative) and $\Delta U < 0$ (negative) $\Longrightarrow$ the system uses its internal energy to supply work to the outside environment (note here that $W_{\text{env}} > 0$ as a result of this).

ii) If the system requires work from the environment, $W > 0$ (positive) and $\Delta U > 0$ (positive) $\Longrightarrow$ the environment supplies work (hence $W_{\text{env}} < 0$) to the system and increases the systems internal energy as a result.

iii) An ideal gas undergoing an adiabatic process obeys the following relation:

$$PV^{\gamma} = \text{ constant} \qquad \text{(XIV-10)}$$

with

$$\gamma = \frac{C_p}{C_v} \ , \qquad \text{(XIV-11)}$$

where γ is called the **adiabatic index** of the gas. See Table 12.1 in the textbook for values of C_p, C_v, and γ for various species.

c) **Isothermal processes**: Temperature does not change during the process. Processes that occur gradually can be considered isothermal since the temperature changes very slowly during the process. In isothermal processes, $\Delta U = 0$ and Eq. (XIV-1) becomes:

$$W = -Q \qquad \text{(isothermal processes)}.$$

i) Using calculus (which we won't show here), it can be shown that the work done on the environment during an isothermal process is

$$W_{\text{env}} = nRT \ln\left(\frac{V_f}{V_i}\right) , \qquad \text{(XIV-12)}$$

where 'ln' is the natural log function.

ii) Since work on the system is just the negative of work on the environment

$$W = -nRT \ln\left(\frac{V_f}{V_i}\right) . \qquad \text{(XIV-13)}$$

d) **Isochoric processes** (also called **isovolumetric processes**): Volume does not change during the process. Since volume does not change, no work can be done on the system. As such, Eq. (XIV-1) then becomes

$$\Delta U = Q \qquad \text{(isochoric processes)}.$$

i) In an isochoric process, the change in thermal energy of a system equals the energy transferred to the system by heat.

ii) From Eq. (XIV-5), the energy transferred by heat in constant volume processes is given by

$$Q = nC_v\Delta T . \qquad \text{(XIV-14)}$$

8. **Enthalpy**: Heat energy associated with phase changes.

   a) Through the use of the 1st law of thermodynamics, we can introduce a new state variable associated with phase changes.

   b) Eq. (XII-12) showed the heat liberated (or needed) during a phase change is related the latent heat. Usually, there is also a volume change when matter changes from one state to another. A volume change results in work either being performed on or by the system via Eq. (XIV-2). Using this equation, along with Eq. (XII-12), in the 1st law (*i.e.*, Eq. XIV-1), we can write

   $$U_2 - U_1 = mL - P\left(V_2 - V_1\right) \ . \qquad \text{(XIV-15)}$$

   i) Solving this equation for the latent heat term gives

   $$mL = (U_2 + PV_2) - (U_1 + PV_1) = H_2 - H_1 \ ,$$
   $$\text{(XIV-16)}$$

   where

   $$\boxed{H = U + PV \ ,} \qquad \text{(XIV-17)}$$

   is called the **enthalpy** of the system.

   ii) The enthalpy, H, is another state variable, which is a function of the 3 other state variables: T (through U), P and V.

   c) As can be seen, the latent heat of fusion and vaporization is just the difference of the enthalpy of the two different states of matter on either side of the fusion or vaporization.

9. Up until now, we have considered only processes in which the potential and *macroscopic* kinetic energies of a system remain

XIV–8

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constant. We now relax this constraint to develop the general form of the 1st law of thermodynamics.

a) The work-energy theorem (*i.e.*, Eq. VI-4) says that the work done *on* a system is equal to the change of kinetic energy:

$$\Delta(\text{KE}) = \text{KE}_\text{f} - \text{KE}_\text{i} = W \ . \qquad \text{(XIV-18)}$$

b) This kinetic energy change should be added to the internal energy change to represent the total kinetic energy $\Longrightarrow$ both macroscopically (*i.e.*, "bulk" kinetic energy) <u>and</u> microscopically (*i.e.*, internal energy):

$$\Delta U + \Delta(\text{KE}) = Q + W \ . \qquad \text{(XIV-19)}$$

c) If conservative forces act on the system, the work done by the conservative forces, W_c, is related to a change in the potential energy through Eq. (VI-6):

$$W_c = -\Delta(\text{PE}) \ . \qquad \text{(XIV-20)}$$

d) Note that the total work done on a system is the sum of the work due to conservative forces and non-conservation forces (labeled with W_{nc}):

$$W = W_c + W_{nc} \ . \qquad \text{(XIV-21)}$$

e) Using Eq. (XIV-21) along with Eq. (XIV-20) in Eq. (XIV-19) we can write

$$
\begin{aligned}
\Delta U + \Delta(\text{KE}) &= Q + (W_c + W_{nc}) \\
&= Q + W_c + W_{nc} \\
\Delta U + \Delta(\text{KE}) - W_c &= Q + W_{nc} \\
\Delta U + \Delta(\text{KE}) + \Delta(\text{PE}) &= Q + W_{nc} \qquad \text{(XIV-22)}
\end{aligned}
$$

f) Now if we define the *total* energy, E, of the system as the sum of the internal energy, the kinetic energy, and the

potential energy,

$$E = U + \text{KE} + \text{PE} , \qquad\qquad \text{(XIV-23)}$$

then we can write the **general form of the first law of thermodynamics** as

$$\boxed{\Delta E = E_\mathrm{f} - E_\mathrm{i} = Q + W_{nc} ,} \qquad\qquad \text{(XIV-24)}$$

noting that if both the kinetic energy and potential energy are constant, then $\Delta E = \Delta U$ and $W_{nc} = W$ which gives us the standard form of the 1st law as written in Eq. (XIV-1).

Example XIV–1. A movable piston having a mass of 8.00 kg and a cross-sectional area of 5.00 cm^2 traps 0.200 mol of an ideal gas in a vertical cylinder. If the piston slides without friction in the cylinder, how much work is done *on* the gas when its temperature is increased from 20°C to 300°C?

Solution:

For an ideal gas as the temperature increases, the volume increases by

$$\Delta V = V_\mathrm{f} - V_\mathrm{i} = \frac{nRT_\mathrm{f}}{P_\mathrm{f}} - \frac{nRT_\mathrm{i}}{P_\mathrm{i}} .$$

Assume the pressure is held constant, $P_\mathrm{i} = P_\mathrm{f} = P$, so we can write

$$\Delta V = \frac{nR}{P}(T_\mathrm{f} - T_\mathrm{i}) = \frac{nR(\Delta T)}{P} .$$

The change in temperature is

$$\Delta T = (300 + 273) \text{ K} - (20 + 273) \text{ K} = 280 \text{ K} .$$

The work done on the gas is

$$W = -P(\Delta V) = -nR(\Delta T) = -(0.200 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(280 \text{ K})$$

$$= \boxed{-465 \text{ J} .}$$

Example XIV–2.   A thermodynamic system undergoes a process in which the internal energy decreases by 500 J. If at the same time 220 J of work is done on the system, find the energy transferred to or from it by heat.

Solution:

From the first law as given in Eq. (XIV-1),

$$Q = \Delta U + W = (-500 \text{ J}) + (220 \text{ J}) = \boxed{-280 \text{ J}} \ .$$

The negative sign in the result means that energy is transferred *from* the system by heat.

C. Heat Engines.

1. Many of the machines used in our current technology are driven by heat engines (indeed, your own body is a heat engine). A **heat engine** is a device that converts internal energy into some other form of energy (*e.g.*, electricity, mechanical [kinetic] energy, etc.).

2. Let's represent a typical heat engine as a cylinder with a piston in it. The total work done by a heat engine is then the net heat flow into the cylinder via the 1st law of thermodynamics (note that $\Delta U = 0$ for the complete cycle):

$$W = |Q_H| - |Q_C| \ , \qquad\qquad \text{(XIV-25)}$$

where $|Q_H|$ is the magnitude (hence a positive number) of the heat that flowed into the system (*i.e.*, engine) and $|Q_C|$ is the magnitude (hence a positive number) of the heat that flowed out of the system.

3. Reversible versus non-reversible processes:

a) A process is said to be **reversible** if the final state of a process can be returned to its initial state.

  i) No dissipative effects that convert mechanical energy to thermal energy (*i.e.*, friction).

  ii) Such processes are nearly impossible to achieve in nature.

b) A process is **irreversible** if the final state of a process cannot be returned to its initial state $\Longrightarrow$ nature behaves in this manner.

4. The **thermal efficiency** e of any system is the ratio of the work done to the heat input:

$$\boxed{e = \frac{W}{|Q_H|}} \, . \qquad\qquad \text{(XIV-26)}$$

a) Using Eq. (XIV-25), we immediately see that

$$e = \frac{|Q_H| - |Q_C|}{|Q_H|} \, . \qquad\qquad \text{(XIV-27)}$$

b) Kelvin showed through the ideal gas law that

$$\frac{|Q_C|}{|Q_H|} = \frac{T_C}{T_H} \, , \qquad\qquad \text{(XIV-28)}$$

where these temperatures are measured in K.

c) Using Eq. (XIV-28) in Eq. (XIV-27), we see that the thermal efficiency of an *ideal* heat engine is

$$e = 1 - \frac{T_C}{T_H} \qquad \text{(ideal engine)}. \qquad\qquad \text{(XIV-29)}$$

d) As can be seen from this, even with an ideal engine (one with no internal friction), it is impossible to make a 100% efficient engine $\Longrightarrow$ it is a physical impossibility to make a *perpetual motion machine* (machines that require no energy to run and never run down).

5. There are two things to always keep in mind when doing calculations with heat engines:

a) W is <u>positive</u> (and W_{env} is negative) when the system <u>contracts</u> (*i.e.*, $\Delta V < 0$), and <u>negative</u> (and W_{env} positive) when it <u>expands</u> (*i.e.*, $\Delta V > 0$).

b) Q is <u>positive</u> for heat <u>coming into</u> the system and <u>negative</u> for heat <u>leaving</u> the system.

Example XIV–3. The energy absorbed by an engine is three times greater than the work it performs. (a) What is the thermal efficiency? (b) What fraction of the energy absorbed is expelled by the cold reservoir?

Solution (a):

Using Eq. (XIV-26) and the fact that $|Q_H| = 3W$, the thermal efficiency is

$$e = \frac{W}{|Q_H|} = \frac{W}{3W} = \boxed{\frac{1}{3} = 0.333 \text{ or } 33.3\%} \ .$$

Solution (b):

Using Eq. (XIV-27) we can write

$$e = \frac{|Q_H| - |Q_C|}{|Q_H|} = 1 - \frac{|Q_C|}{|Q_H|}$$

$$\frac{|Q_C|}{|Q_H|} = 1 - e$$

$$= 1 - \frac{1}{3} = \boxed{\frac{2}{3}} \ .$$

D. The Carnot Cycle.

1. In the early 1800s, Carnot pointed out the basic working of an *ideal* (one without internal friction) heat engine.

2. The **Carnot cycle** (see Figure 12.18 in your textbook) can be described in 4 steps:

a) **Step 1**: The cycle starts with the piston positioned such that V is at a minimum. At this point, heat Q is added to the system through a heat reservoir at a high temperature T_H. The system absorbs the heat a constant temperature T_H which causes the volume to expand doing work on the piston. During this time, the system's internal energy does not change ($\Delta U = 0$) and since T is not changing, it is an isothermal process. From the 1st law of thermo, the work done <u>by</u> the system ($W < 0$) is equal to the negative of the heat input Q_H.

b) **Step 2**: The cylinder is moved off of the heat reservoir onto an insulator. This isolates the heat in the system which makes this step adiabatic. The load on the piston is reduced which allows the gas to expand in the cylinder (hence the volume continues to increase). This expansion of gas does work on the system (which is the same thing as saying that the work is done <u>by</u> the system, $W < 0$) causing the internal energy to go down (since Q is constant here). During this phase of the expansion, the temperature decreases.

c) **Step 3**: The cylinder is then moved to a heat sink at a cooler temperature T_C. The internal heat flows out Q_C of the system at constant temperature (hence an isothermal process). The volume decreases which causes work to be

done <u>on</u> the system ($W > 0$).

d) **Step 4**: The cylinder is moved back to the insulator. The load on the piston is increased and the gas undergoes adiabatic compression. Since volume is still decreasing, work is still being done <u>on</u> the system ($W > 0$). The internal energy returns to the value that it had at the start of Step 1.

3. The Carnot engine is said to be a "reversible" engine.

E. Refrigerators and Heat Pumps.

1. Reversing the Carnot cycle, we can put work into a system and transfer heat from a lower temperature to a higher one $\Longrightarrow$ a **refrigerator**.

   a) The heat extracted from the cold reservoir to the work supplied (similar to the thermal efficiency) is called the **coefficient of performance** η:

$$\eta_{\text{frig}} = \frac{Q_C}{W} \ . \qquad\qquad \text{(XIV-30)}$$

   b) Using Eq. (XIV-25) and Eq. (XIV-28), we can write

$$\eta_{\text{frig}} = \frac{|Q_C|}{|Q_H| - |Q_C|} = \frac{T_C}{T_H - T_C} \ . \qquad \text{(XIV-31)}$$

2. Air conditioners are refrigerators that move heat from within a house to outside a house.

3. The reverse of an air conditioner is a **heat pump** $\Longrightarrow$ it cools the outdoors by delivering heat from the outdoors to the inside.

   a) The coefficient of performance for a heat pump is given by

$$\eta_{\text{hp}} = \frac{Q_H}{W} \ . \qquad\qquad \text{(XIV-32)}$$

b)   Using Eq. (XIV-25) and Eq. (XIV-28), we can write

$$\eta_{\text{hp}} = \frac{|Q_H|}{|Q_H| - |Q_C|} = \frac{T_H}{T_H - T_C} \; . \qquad \text{(XIV-33)}$$

F. The Second Law of Thermodynamics — The Classical Description.

1.   The second law of thermodynamics deals with how heat flows. It is essentially a description of *change*.

a)   **Change**: To make different the form, nature, and content of something.

b)   Change has, over the course of time and throughout all space, brought forth, successively and successfully, galaxies, stars, planets, and life.

c)   Evidence for change is literally everywhere.

   i)   In the macroscopic domain as viewed through telescopes: The Universe started out being fairly homogeneous (*i.e.*, the same everywhere) until today it is very inhomogeneous. Heavy elements (*i.e.*, C, N, O, Fe, etc.) have become more abundant over time. Stars have formed from a few billion years after the Big Bang until the present epoch (and will continue to form in the far distant future).

   ii)   In the mesoscopic domain as deduced from geologic records and via microscopes studying the biological world.

   iii)   And in the microscopic domain as studied with high-energy particle accelerators.

d) Much of the change is subtle, such as when the Sun fuses hydrogen into helium sedately over billions of years or when the Earth's tectonic plates drift sluggishly across the face of our planet over those same billions of years.

e) Indeed, our perception of time is nothing more than our noticing changes on Earth and in the Universe as a whole.

2. There are two classical formulations of this law (both essentially mean the same thing):

a) Clausius statement of the second law: Heat cannot, by itself, pass from a colder to a warmer body.

b) Kelvin-Planck statement of the second law: It is impossible for any system to undergo a cyclic process whose *sole* result is the absorption of heat from a single reservoir at a single temperature and the performance of an equivalent amount of work.

3. The 2nd law specifies the way in which *available energy* (also called "usable energy," "free energy," or "potential energy") change occurs.

a) This law's essence stipulates that a price is paid each time energy changes from one form to another.

b) The price paid (to Nature) is a loss in the amount of available energy capable of performing work of some kind in the future.

c) We define here a new term to describe this decrease of available energy: *entropy*, S. It is derived from the Greek word *tropae* which means "transformation."

4. The second law of thermodynamics is different from the laws of mechanics. It does not describe the interactions between individual particles, but instead describes the overall behavior of collections of many particles.

a) In classical mechanics, an event is symmetrical in time $\Longrightarrow$ the laws are satisfied whether we run the experiment forward or backward in time.

b) The second law tells us about the sequence, or order, in which events naturally take place $\Longrightarrow$ **the second law of thermodynamics shows us the direction in which time progresses**.

5. The concept of entropy.

a) Clausius introduced a new state variable called entropy.

b) As defined above, **entropy** is a measure of how much energy or heat is u̲n̲available for conversion into work.

c) When a system at temperature T (in K) undergoes a *reversible* process by absorbing an amount of heat Q, its increase in entropy ΔS is

$$\boxed{\Delta S \equiv \frac{\Delta Q}{T} = \frac{Q}{T}} \qquad \text{(XIV-34)}$$

where often we simply write Q for the heat input or removed instead of the more proper form of ΔQ.

i) If $Q > 0 \Longrightarrow$ heat is absorbed by the system $\Longrightarrow$ entropy increases.

ii) If $Q < 0 \Longrightarrow$ heat is expelled by the system $\Longrightarrow$ entropy decreases.

iii)   For reversible processes, $Q = 0$ and the entropy change is zero.

d)   As can be seen by Eq. (XIV-34), entropy, when multiplied by temperature, is a measure of the amount of energy, Q, no longer capable of conversion in useful work.

e)   We can use this concept of *unavailable energy* versus *available energy* to develop a different form for the first law of thermodynamics. We can express the total energy E (see Eq. XIV-23) as

$$E = F + TS \ , \qquad\qquad \text{(XIV-35)}$$

where TS (*i.e.*, temperature times entropy) represents the energy that is unavailable to be converted to work and F, called the **Helmholtz free energy**, is the energy available to be converted to work.

i)   The first law can then be written by making this a difference equation:

$$\Delta E = \Delta F + T\Delta S + S\Delta T \ , \qquad \text{(XIV-36)}$$

where we have made use of the "product rule" from differential calculus for the TS term.

ii)   Eq. (XIV-36) shows that if the temperature change over time is small or zero (which is typically the case for an isolated or closed system), the conservation of energy dictates that as free energy decreases the energy unavailable for conversion to work increases $\Longrightarrow$ the entropy increases.

iii)   To demonstrate this mathematically, let $\Delta E = 0$ (*i.e.*, the conservation of energy), then Eq. (XIV-

36) becomes:

$$0 = \Delta F + T\Delta S + S\Delta T ,$$
$$\Delta F = -T\Delta S - S\Delta T .$$

Since both terms on the right-hand side of the above equation are negative, the *free energy F*, or energy available to do work, decreases in time, which means that the *entropy*, or energy <u>unavailable</u> to do work, must increase as stated above.

iv) Given enough time, all closed systems will "run down" until they are capable of performing no more work $\Longrightarrow$ once again, it is impossible to make a perpetual motion machine!

G. The Second Law of Thermodynamics — The Probabilistic Description.

1. In the late 1800s, Boltzmann showed that an increase in entropy of a system corresponds to an increased degree of *disorder* in the atoms or molecules composing the substance.

a) This realization lead to the creation of a new area of physics known as **statistical mechanics** which rewrites the laws of thermodynamics in a probabilistic formalism.

b) Boltzmann rewrote the entropy equation definition in terms of a probability equation:

$$S = k_{\mathrm{B}} \ln W , \qquad \text{(XIV-37)}$$

where k_{B} is Boltzmann's constant, 'ln' is the natural logarithm of base 'e', and W is the number of different arrangements of microscopic states (*i.e.*, positions, velocities, compositions, and any various arrangements of quan-

tum properties). **Note that W here does <u>not</u> mean work!**

i)   Boltzmann actually has Eq. (XIV-37) carved on his gravestone in Vienna!

ii) W is a measure of the inverse probability, p, of the occurrence of the possible microscopic states a system can have.

iii) That is, $p = 1/W = 1$ for a 100% chance $\Longrightarrow$ Then it is completely certain that a process will occur when $p = 1$.

iv) As a result, we could also write the definition of entropy (*i.e.*, Eq. XIV-37) as

$$S = k_{\mathrm{B}} \ln \left(\frac{1}{p}\right) = -k_{\mathrm{B}} \ln p \; . \qquad \text{(XIV-38)}$$

c)   With the help of Eq. (XIV-38) we can see the second law implies that any <u>isolated</u> system naturally tends towards an equilibrium state of minimum microscopic probability — namely, a uniformity of temperature, pressure, chemical composition, and so on.

i)   Since ordered molecular states (for example, where molecules in one part of the system have one property value, but those in the remaining part have another) are less probable than those of random or disordered states.

ii) Boltzmann's law of entropy then signifies that ordered states tend to degenerate into disordered ones in a <u>closed</u> system.

d) As can be seen, the concept of "disorder" is very difficult since it requires a detailed knowledge of probability and statistics.

i) The best way to learn about probabilities is through example. Let's say we have one die from a set of dice. There are 6 sides with dots imprinted on the sides relating to the numbers 1, 2, 3, 4, 5, and 6.

ii) The probability of one number (say '4') coming up is

$$p = \frac{n}{N} = \frac{\text{a given state}}{\text{total number of states}} \ , \qquad \text{(XIV-39)}$$

and for this case, $n = 1$ and $N = 6$, so

$$p = \frac{\text{one side}}{\text{total number of sides}} = \frac{1}{6} = 0.167 \ ,$$

or a 16.7% chance that we would role the die with a '4' landing on top.

iii) The probability of an even number (2, 4, or 6) landing on top is ($n = 3$ and $N = 6$)

$$p = \frac{3}{6} = 0.50 \ ,$$

or a 50% chance to role such a number.

2. Through this concept of entropy, we can rewrite the second law of thermodynamics as any of the following statements:

a) The entropy of the Universe as a whole increases in all natural processes.

b) Isolated systems tend towards greater disorder and entropy is a measure of that disorder.

    c)   In a closed system, entropy increases over time $\Longrightarrow$ less and less energy can be converted into work.

    d)   All of these statements are probabilistic in nature $\rightarrow$ on average these statements are true.

3. Note that the second law written in this probabilistic way can be violated locally $\Longrightarrow$ entropy can decrease locally. Only over the whole isolated (or closed) system over a long enough period of time, will necessitate an increase in entropy.

    a)   Note that on the Earth, entropy decreases all the time at the expense of an increase of entropy of the Sun.

    b)   As such, the second law of thermodynamics <u>cannot</u> be used as proof <u>against</u> the theory of biological evolution as some people have suggested.

4. The bottom line is that we no longer regard things as "fixed" or "being," or even that they "exist." Instead, everything in the Universe is "flowing," always in the act of "becoming." All entities — living and non-living alike — are permanently changing.

Example XIV–4.   A 70.0-kg log falls from a height of 25.0 m into a lake. If the log, the lake, and the air are all at 300 K, find the change of entropy of the Universe for this process.

Solution:

The potential energy lost by the log is carried away by heat, that is, the kinetic energy of the impact into the lake get converted into heat, so

$$
\begin{aligned}
\Delta Q &= \Delta(\text{PE}) = mg\Delta y = mgh = (70.0 \text{ kg})(9.80 \text{ m/s}^2)(25.0 \text{ m}) \\
&= 1.7\underline{1}5 \times 10^4 \text{ J} ,
\end{aligned}
$$

where we have carried along an extra digit to reduce round-off error in the solution below. We will ignore air friction here and since the temperature remains constant, we just have one term in the entropy equation. As such, the change of entropy is

$$\Delta S = \frac{\Delta Q}{T} = \frac{1.7\underline{1}5 \times 10^4 \text{ J}}{300 \text{ K}} = 57.\underline{1}67 \text{ J/K} = \boxed{57.2 \text{ J/K}} \, .$$