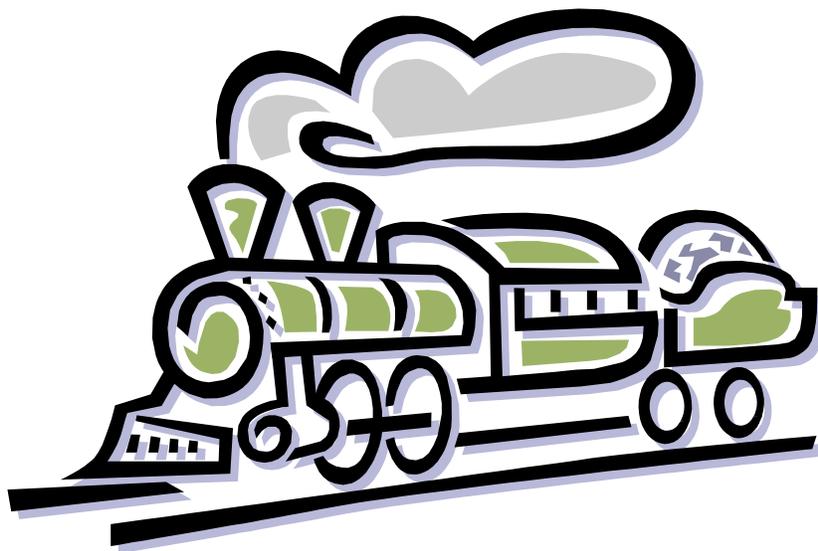


Thermodynamics

Unit 202



This is the second of two units on the study of Thermodynamics. In this unit we look at some of the laws that came about due to the study of steam engines, internal combustion engines and chemical reactions. There are actually 4 laws of thermodynamics if you count the zeroth law. We will focus upon the 1st and 2nd laws in this unit. By the time we finish this unit we will have completed two of the five major areas of physics. Before taking a test on this unit a student should be familiar with all of the areas described in the following outline.

I. First Law of Thermodynamics

A. Internal Energy

B. Work Done by a Gas

C. Heat Flow into a Gas

II. Gas Cycles

A. Net Work for the Cycle

B. Net Heat for the Cycle

C. Actual Efficiency for the Cycle

III. Second Law of Thermodynamics

A. The Carnot Cycle and Maximum Efficiency

B. Entropy

Read Sections 12.1-12.3

The entire idea behind a steam engine is to take the kinetic energy of each individual atom in a gas and convert it into the kinetic energy of the locomotive. Granted each little molecule has a very tiny amount of KE but when you have a mole or two of particles their combined kinetic energies can add to a significant amount. The First Law of Thermodynamics tells us how to consider the internal energy of the gas, the work done on the gas and the heat that flows into the gas.

Look at the picture on the cover sheet of this unit. Behind the locomotive is the coal car. The fireman inside of the cab shovels coal into the stove. Burning the coal generates a source of heat, Q . The heat will flow from the stove into the big cylindrical tank of water that sits above the wheels and below the smokestacks. This heat flow into the water makes the particles move faster generating steam. As the water molecules move faster they gain the internal kinetic energy, U . Just in front of and even with the front wheels sits a piston. The steam inside of the tank builds pressure. The expanding gas can push the piston backwards doing work, W via force times distance, to turn the wheels and move the locomotive. In this lesson we will look at each of the types of energy, Q , U and W in turn. They are all related by the algebraic expression of the first law shown in the text box to the right.

First Law of Thermodyn.

$$\Delta U = Q + W$$

Internal Energy of the Gas

If the gas particles are not moving then the locomotive cannot go. The kinetic energy of all gas particles is found by calculating the total internal energy of the gas. The ideal scenario for any engine is that as the internal energy decreases that energy is being turned into useful work. The most direct way to find the change in internal energy is shown to the right. We can also write equations for the change in internal energy for special processes.

Internal Energy Change

$$\Delta U = U_f - U_o$$

Isobaric Process

$$\begin{aligned}\Delta U &= 3/2 P \Delta V \\ &= (3/2)P(V_f - V_o)\end{aligned}$$

Isochoric Process

$$\begin{aligned}\Delta U &= 3/2 \Delta P * V \\ &= 3/2(P_f - P_o)V\end{aligned}$$

Isothermal Process

$\Delta U = 0$ since constant temperature means no change in particle speed.

Adiabatic Process

$$\begin{aligned}\Delta U &= 3/2 n R \Delta T \\ &= (3/2)nR(T_f - T_o)\end{aligned}$$

All of the above equations come from the definitions of internal energy in chapter 10. There we saw that $U = 3/2 PV$ or $3/2 nRT$ or $3/2 NkT$. Note that the expression for the adiabatic process happens to be true for any other cases as well.

Work Done by the Gas

Now we get to a great controversy between the engineers and chemists. All work done by or on a gas takes place only as the gas changes volume. The engineers like for the gas to expand so that the piston can turn the wheel of the locomotive. See figure 12.1 to get an idea how a piston works. So engineers want to have positive work take place for a gas with increasing volume ($+W$ if Volume \uparrow). Chemists on the other hand recognize that expanding gases seem to slow chemical reactions. They decided that work is negative for increasing volume ($-W$ if Volume \uparrow). If you take certain chemistry courses and

engineering courses at the same time, beware. By convention in this course we will use contracting volume to be defined as positive work. If a gas expands or the graph moves to the right the work done is negative. If the gas contracts or a graph moves to the left the work done is positive. If the volume of a gas does not change, an isochoric process, the work done is zero. See figures 12.2, 12.3 and 12.4 for finding work from a graph.

<u>Isobaric Process</u>	<u>Isochoric Process</u>	<u>Isothermal Process</u>	<u>Adiabatic Process</u>
$W = -P \Delta V$ $= -P (V_f - V_o)$	$W = 0$ since the volume is constant.	$W = -Q$ One of these must be given due to the calculus nature of the curve. You could use $W = nRT \ln(V_f/V_o)$	$W = \Delta U$ $= 3/2 n R \Delta T$ Area under this curve is also tricky. Try [2 nd],[TRACE], [7]?
Area under graph is a rectangle.	There is no area below a vertical line.		

The expression for the work done under the isothermal process is complicated by the fact that the graph is a curve. The adiabatic process is also a curve. In either case you cannot find the area under the curve unless you know calculus or if you know the equation for the P-V graph you can use the graphing calculator. See figure 12.4 (c) for example.

On AP exams they usually give you the W or the Q for the isothermal process and count on you, the student to recognize that they are equal. Stop and appreciate the beauty of the isothermal process. As fast as the boiler is dumping heat into the steam, the piston is doing equal amount of work out at the other end. In other words, a perfect conversion of heat to work, hence $-W = Q$. This is the most efficient process for any engine.

Although the work done during the adiabatic step is also a complicated, calculus curve you can still figure it out without any help. During this step no heat flows into the steam from the stove, hence $Q = 0$. All of the work done at this point comes from kinetic energy of the gas particles in the cylinder. As the gas does work pushing the piston it is losing internal energy during the process, hence $-W = -\Delta U$. Parts of the cycle in the internal combustion engines use this process.

Heat Flow into a Gas

By now you should realize that heat flow into the gas does one of three things. The heat can increase the internal energy in the gas. The heat can be converted to useful work. Or sadly enough the heat can leak out of the system. Since heat loss means less energy available to drive a chemical reaction we continue to use the chemistry convention that heat flow into the gas is positive while heat flow out of the gas is negative. We have already discussed heat flow in the previous unit. In this unit we will use a calculation of heat that is similar to specific heat except that it discusses heat in terms of moles rather than kilograms. The old equation containing $Q = mc \Delta T$ that used the specific heat will now be replaced with $Q = n C \Delta T$. The “C” goes by heat capacity and funny things were noticed about the heat capacity of gases. The value of C for a gas depends on if it is measured at constant pressure (C_p) or if it is measured at constant volume (C_v). All noble gases had the same C_v value, $3/2 R$ and the same C_p value, $5/2 R$. These values did not agree with the heat capacity of diatomic gases like hydrogen, oxygen and nitrogen however. All diatomic gases have heat capacity values of $C_v = 5/2 R$ and $C_p = 7/2 R$. Polyatomic gases like steam and methane have $C_v = 6/2 R$ and $C_p = 8/2 R$. You won’t be held responsible for knowing these values on the test or AP Exam but at least recognize some of the following facts. Instead of a specific heat value for every individual substance we have two heat capacity values, C_v and C_p . There are only six of these values that we need to keep up with

rather than a different number for every kind of gas. The values are all multiples of R and are expressed in terms of moles rather than in terms of kilograms or particles which is why the $PV=nRT$ version of the ideal gas law is most commonly used. Your biggest concern is using the C_V when you are working a constant volume process rather than a C_P . The AP exam writer will furnish you with both values. It turns out that there is a perfectly good explanation as to why the numbers change from noble gases to diatomic to polyatomic but that is not required for this course. The values are listed in a table for your convenience. We should list the methods for each of special processes.

Gas	C_V	C_P
noble	$3/2 R$	$5/2 R$
diatomic	$5/2 R$	$7/2 R$
polyatm	$6/2 R$	$8/2 R$

Isobaric Process

$$Q = n C_P \Delta T$$

$$= n C_P (T_f - T_o)$$

Isochoric Process

$$Q = n C_V \Delta T$$

$$= n C_V (T_f - T_o)$$

Isothermal Process

$-W = Q$ and one of these two must be given.

Adiabatic Process

By definition $Q = 0$.

As mentioned in the last unit, there are six ways to determine the heat flow. Four of them were described. We can now add to that list the use of the first law of thermodynamics to calculate Q . The first law merely recognizes that heat is another form of energy. It does not tell us anything about which way heat must flow. Can it flow from hot to cold as well as from cold to hot? Clearly we need more than the Zeroth law and the First law.

Homework Problems 12: 3, 5, 6(part b should read “from P_1 to P_2), 7, 8, 9, 10, 13, 14, 15, 17, 19, 22

Lesson 2-11 Gas Cycles

Review pages 6-8 of the previous unit

For most engines including steam engines, gasoline engines and diesel engines some gas is taken through a complete cycle and then vented out of the piston. The old gas is replaced with the new gas and the cycle repeats. For the gasoline and diesel engines the heat source is a chemical reaction of the gas with oxygen that takes place while the gas is inside of the piston. The different things that happen to the gas during the cycle will influence the shape of the P-V diagram. In any case we at least recognize that at the end of the cycle the gas is back at the beginning forming a closed loop. You have already seen three examples of a gas cycle on pages 6-8 of the previous unit. We can now add to the values found in the chart for those problems a second chart. Before we go back and add the second chart to those problems we must acknowledge a few important facts.

1. The final temperature for a cycle is the same as the initial temperature in a cycle. This means the change in internal energy for an entire cycle is always zero.

$$\Delta U_{\text{CYCLE}} = 0$$

2. The net work done by a gas during a complete cycle is equal to the area surrounded by the P-V graph. See figure 12.6. Clockwise cycles create negative net work.

3. The net flow of heat into and out of a gas during a cycle equals the net work done by the gas according to the 1st Law of Thermodynamics.

$$Q_{\text{CYCLE}} = -W_{\text{CYCLE}}$$

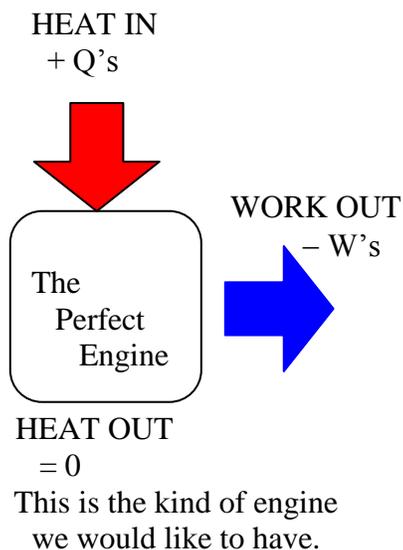
4. The actual or real efficiency of any engine is the ratio of the work done during a complete cycle divided by the positive heat flow into the engine. Think about it. A perfectly efficient engine would convert every single Joule of heat to useful work with no heat wasted. You can multiply by 100 to get a percent. Compare figures at bottom of this page.

$$\text{Actual eff.} = 100 * W_{\text{CYC}} / +Q's$$

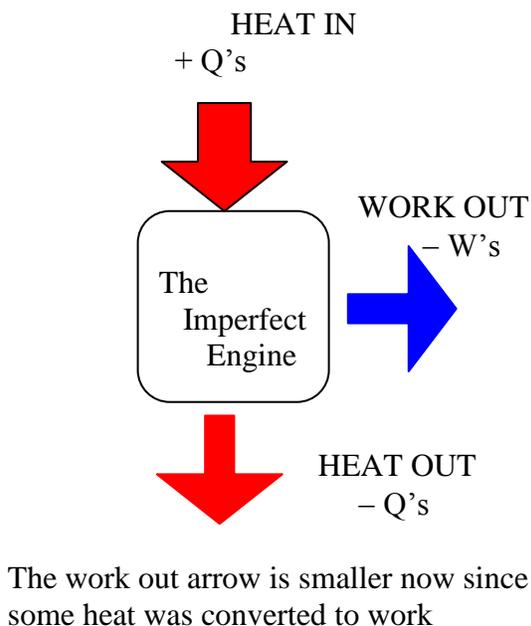
In today's lesson we will complete the following chart for each of the gas cycles shown on pages 6-8 of the previous unit. Each row in this chart represents a step in the cycle rather than a point in the cycle. We will also use the bottom of the chart to find the actual efficiency of each of the cycles.

Step	ΔU (kilojoules)	Q (kilojoules)	W (kilojoules)	ΔS^* (kilojoules/ K)
A – B				
B – C				
C – A				
Cycle				

A Perfect Heat Engine

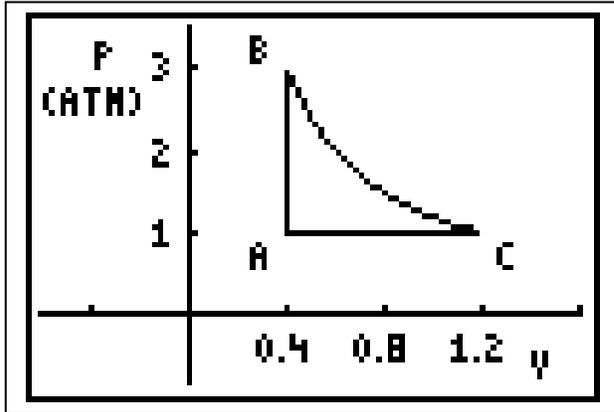


An Actual Heat Engine



Gas Cycle #1

One mole of an ideal, monatomic gas starts at 1 atmosphere and 0.4 m³. The gas triples in pressure at during an isochoric process. The gas then drops in pressure under an iso-thermal process back to its original pressure. Finally, the gas contracts under an isobaric process back to the original volume. During step B-C the gas does 133.2 kilojoules of work.



Point	P (kPa)	V (m ³)	T (K)	U (kJ)
A				
B				
C				

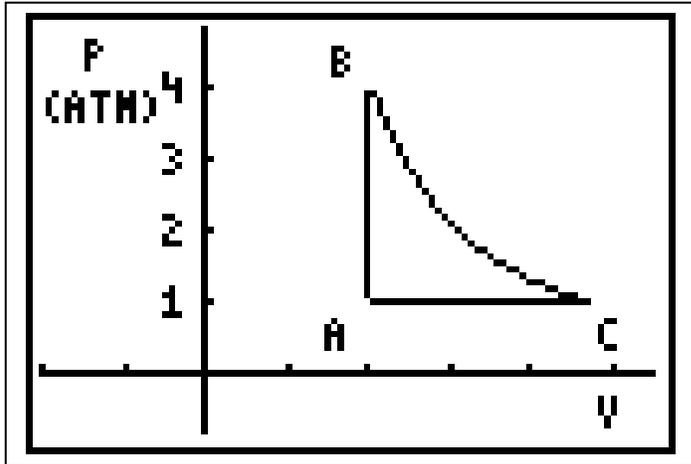
Real Efficiency = _____%

Step	ΔU (kilojoules)	Q (kilojoules)	W (kilojoules)	ΔS^* (kilojoules/ K)
A – B				
B – C				
C – A				
Cycle				

In the space to the right of the P-V diagram draw your heat engine diagram showing all of the heat flow into and out of the system and the net work done for the cycle. Also determine the actual efficiency of this engine.

Gas Cycle #2

A $1/10$ mole of an ideal, monatomic gas starts at 1 atmosphere and 0.0041 m^3 . The gas pressure quadruples during an isochoric process. The gas then drops in pressure under an adiabatic process back to its original pressure and a volume of 0.0094 m^3 . Finally, the gas contracts under an isobaric process back to the original volume.



Point	P (kPa)	V (m^3)	T (K)	U (kJ)
A				
B				
C				

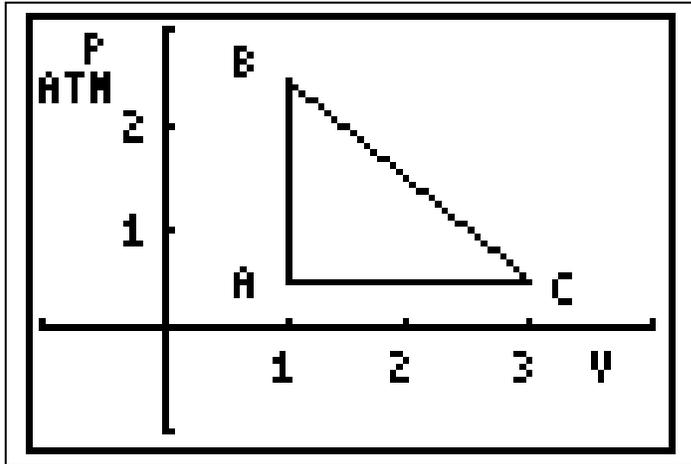
Real Efficiency = _____%

Step	ΔU (kilojoules)	Q (kilojoules)	W (kilojoules)	ΔS^* (kilojoules/ K)
A – B				
B – C				
C – A				
Cycle				

In the space to the right of the P-V diagram draw your heat engine diagram showing all of the heat flow into and out of the system and the net work done for the cycle. Also determine the actual efficiency of this engine.

Gas Cycle #3

A $1/50$ mole of an ideal, monatomic gas starts at $1/2$ atmosphere and 1.00 m^3 . The gas pressure increases to 2.5 atm by an isochoric process. The gas then expands under a linear process to a volume of 3.0 m^3 and its original pressure. Finally, the gas contracts under an isobaric process back to the original volume.



Point	P (kPa)	V (m ³)	T (K)	U (kJ)
A				
B				
C				

Real Efficiency = _____%

Step	ΔU (kilojoules)	Q (kilojoules)	W (kilojoules)	ΔS^* (kilojoules/ K)
A – B				
B – C				
C – A				
Cycle				

In the space to the right of the P-V diagram draw your heat engine diagram showing all of the heat flow into and out of the system and the net work done for the cycle. Also determine the actual efficiency of this engine.

Homework Problems 12: Complete these cycles

Lesson 2-12 The Carnot (pronounced “Car-no”) Cycle and Maximum Efficiency

Read 12.5-12.6

Up to this point one may be wondering what the shape of the most efficient cycle is. We have seen that rectangular cycles and triangular cycles are not 100% efficient. Even a circular PV diagram is not perfect. So what is the shape of the most perfect gas cycle? In an attempt to answer this questions a Frenchman, Sadi Carnot, considered two special processes. By combining these processes we arrive at the most efficient cycle, now known as “The Carnot Cycle”. Before looking at that cycle lets review the two special processes.

- The isothermal process is definitely the most efficient of all possible steps. During the isothermal process the internal energy does not increase. Every Joule of heat coming into a gas is converted to useful work or vice-versa.
- The adiabatic process is also a fairly efficient step. There is no heat loss during this step. Here instead of heat getting converted to useful work it is the molecular motion of the gas particles that gets turned into work. During adiabatic steps internal energy turns into work or vice-versa.

The Carnot Cycle is a 4 step cycle using alternating processes of isotherms and adiabats. The cycle is described on pages 373 to 374. It was soon realized that this cycle is the most efficient of all cycles. Using the cycle we can construct an expression for the efficiency in terms of the hottest temperature and the coldest temperature in the cycle. This efficiency is shown in the box to the right. It is now known as the Carnot Efficiency. The temperatures in the box are the hottest and coldest temperatures present in the cycle.

$$e_{\text{CARNOT}} = (T_{\text{H}} - T_{\text{C}}) / T_{\text{H}} * 100$$

T's must be in **Kelvins**.

As a student you may become slightly confused at this point since there are now two different definitions of efficiency. The efficiency on page 5 is the actual or real efficiency of any engine. The efficiency on this page is the upper limit to how good you can improve an engine. If an engineer calculates actual efficiency to be 20% and then notices that the Carnot efficiency is 45% then he/she may wish to take a look at the system design. On the other hand if the actual efficiency is 18% and the carnot efficiency is 20% an engineer may be satisfied that the system is pretty close to operating at the maximum possible efficiency. The text calls the two efficiencies “thermal efficiency” and “carnot efficiency”.

The big news here is that there is only one way to get an engine to operate at 100% efficiency. The value of T_{C} has to be 0 Kelvins to get a perfect engine. This kind of makes sense that a perfect heat engine would draw all of the molecular motion out of the gas. The problem is that so far we have not had the ability to operate at 0 Kelvins. This means there is no such thing as a 100% efficient engine. Study examples 12.9 to 12.9.

Drawing heat engine diagrams is very helpful with efficiency calculations.

Homework Problems 12. 23 - 29, 30, 32, 33 also determine the carnot efficiency for each of the three gas cycles from the last assignment.

Lesson 12-13 Entropy and the Second Law of Thermodynamics

Read 12.7 –12.8

The zeroth law of thermodynamics tells us that it is OK to use thermometers. The first law of thermodynamics is merely a way of recognizing conservation of energy with heat being a form of energy. These two laws do not tell the whole story. If only these two laws dictated the state of the universe our lives would be very different. Consider walking by a small pond in August when suddenly all of the internal energy from the pond water flows out of the pond and into your body. This is not a violation of the 1st Law of Thermo. Of course if this were to happen the pond would become frozen solid and you would be on fire. The reason that you've never seen this event is addressed in the 2nd Law of Thermodynamics. Before getting to the 2nd Law we must define *Entropy*.

Entropy Defined

Entropy is the measure of disorder in the universe. We are all aware that disorder exists in our lives. Clean your room up, wait and see. Throw a deck of playing cards into the air and watch them land. In every natural process in the universe things tend to go from order to disorder. Entropy is the measure of the amount of disorder in the universe. The symbol for entropy is **S**. Entropy is measured in Joules / Kelvin. The reason that you can safely walk beside a pond and not become toasted has to do with entropy. If all of the internal energy left the pond and entered your body there would be an increase in entropy in your system. At the same time the pond is freezing and becoming more ordered. The entropy decrease in the pond would be greater than the entropy increase in your body. But ponds do freeze sometimes. At a certain temperature the internal energy of the pond can escape and allow the pond to freeze. What determines this temperature? It is the temperature below which the increase in entropy of the air is greater than the decrease in entropy of the pond. The temperature happens to be 32° F at 1.0 atm.

Entropy Changes Calculated

In general the entropy of a system is not important. The change in entropy is much more critical. We can calculate a change in entropy for any given process. For the AP exam the two critical processes

$$\Delta S = \Delta Q / T$$

are the isotherm and the adiabat. The general equation for a change in entropy is shown in the box to the right. The trouble with this definition is that T is usually a variable during the process. You either use calculus or approximate by dividing by the mid-point of the temperature range. If you do approximate be sure to use $\Delta S \approx$ rather than $\Delta S =$. During the isotherm T is constant and the above equation works exactly. Phase changes are isothermal by the way. During the adiabat there is no heat flow so $\Delta S = 0$. You are not responsible for the other two but they are listed below.

Isobaric Process

$$\Delta S = nC_P \ln(T_f/T_o)$$

Isochoric Process

$$\Delta S = nC_V \ln(T_f/T_o)$$

Isothermal Process

$$\Delta S = Q / T$$

Adiabatic Process

$$\Delta S = 0$$

since no heat flow

Use the previous equations to calculate changes in entropy for the gas cycles on pp. 6-8.
Homework Problems 12. 35, 36, 37, 38, 39 (note that $S_{\text{SUN}} = 1000\text{J}/5700\text{K}$), 43, 44.

Second Law of Thermodynamics

There are a lot of different ways of stating the second law. Some of the consequences of the second law are listed below.

1. Under natural conditions heat will always flow from high temperature to low temperature unless work is done. This is from the Clausius statement.
2. You cannot have a 100% efficient engine since there will always be some heat rejected. This is from the Kelvin-Planck statement and eliminates perpetual motion possibilities.
3. The Total Entropy of the Universe will always remain constant or increase but never decrease. If entropy decreases in one place it must simultaneously increase somewhere else. I wonder what Albert E. would say about that?

The Mechanical Universe Film series for College has a really nice 30 minutes tape on the 2nd Law. I highly recommend it and I don't usually like to show films.

An anonymous writer once described the laws of thermodynamics as the following:

1. The 0th Law describes temperature equilibrium between objects in contact. Since we are in touch with our surroundings then "*Life is a game we all must play.*"
2. The 1st Law tells us about conservation of energy and that you cannot create something from nothing. We conclude, "*You cannot win. The best that you can do is break even.*"
3. The 2nd Law recognizes the trouble with entropy and disorder. We must admit "*The only way to break even is to live forever.*"
4. The 3rd Law that we did not discuss kind of puts a damper of getting to a temperature of absolute zero. This means "*You cannot live forever.*"

We have come to the end of the second of two units on thermodynamics. There are several more PV diagrams problems in the book. The AP exam usually gives a single thermodynamics free-response problem. Most often it is one of the following:

- a) Gas Cycle with a P-V diagram
- b) A heat engine problem
- c) A calorimetry experiment with perhaps a temperature vs. time graph.

We are now finished with about 50% of the material on the AP exam. Our next topic is Electricity and Magnetism, which covers about another 25% of the exam.