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Second Law and Entropy

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SECOND LAW AND ENTROPY

INTRODUCTION

Suppose you get into your car and drive to _____.* During this trip, (1) the burning of the gasoline in the engine cylinders converts chemical energy into thermal energy of the gases - that is, they become very hot; (2) the expansion of these hot gases turns the crankshaft, performing work; and (3) this work, transmitted to the wheels, gives the car kinetic energy - which must be continually replenished, because of depletion by friction and air resistance. At the end of this trip, _____ gallons of gasoline have been converted into water vapor, carbon dioxide, and sundry less desirable vapors, scattered across _____ miles of countryside. In addition, the road, the air along it, and your engine have been heated up. No energy has been lost, but energy has merely been converted to different forms. So why not somehow collect all that energy again, and use it to drive another engine (presumably of a different kind)? That would not violate the first law of thermodynamics - but try to do it!

Well, then, perhaps we should concentrate just on the operation of the heat engine, step 2 above. Present-day gasoline engines convert only a small fraction of the "heat energy" released in their cylinders into useful work. Since we are being pinched by energy shortages, why not gear up a research program to develop engines with (say) 90% efficiency? Again, this too is impossible!

These are illustrations of the fact that energy is often unavailable (or only partially available) for conversion into work. There is a fundamental limit to the efficiency that can be obtained in this conversion - a limit that cannot be surpassed, regardless of technological developments. The basis of that limit is the subject of this module.

*Student should fill in the blanks as appropriate.

PREREQUISITES

Before you begin this module, you should be able to:	Location of Prerequisite Content
*Write the equation of state of an ideal gas and find one parameter in terms of the others. Know that the internal energy is a function only of the absolute temperature for an ideal gas (needed for Objective 3 of this module)	Kinetic Theory of Gases Module
*Write and evaluate the expression for work done by or on an ideal gas by various processes (needed for Objective 3 of this module)	Temperature, Heat, and Thermodynamics Module
*State and use the first law of thermodynamics; and describe the absolute-temperature (K) scale and how to convert degrees Celsius to kelvins (needed for Objective 3 of this module)	Temperature, Heat, and Thermodynamics Module
*Calculate the specific heat at constant volume for an ideal gas (needed for Objective 3 of this module)	Kinetic Theory of Gases Module
*Solve problems involving the latent heats of fusion and vaporization and specific heat (needed for Objective 3 of this module)	Temperature, Heat, and Thermodynamics Module

LEARNING OBJECTIVES

After you have mastered the content of this module, you will be able to:

1. Definitions - Define the following: (a) reversible process, (b) irreversible process, (c) state variable, (d) cycle, (e) efficiency, (f) Carnot cycle, and (g) entropy.
2. Second law of thermodynamics - State the second law of thermodynamics as it relates to entropy on a macroscopic scale, and show that the second-law statements relating to heat flow satisfy this statement.
3. Entropy - Solve problems involving the following concepts: (a) efficiency and heat cycles from pV diagrams or from information necessary to construct pV diagrams; (b) Carnot cycles; and/or (c) entropy.

GENERAL COMMENTS1. Definitions

The important definitions to know for this module are the following:

(a) Reversible process: a process that, by a differential change in the environment, can be made to retrace its path. Note: reversible processes can be represented graphically since at any time the system is (essentially) in equilibrium.

(b) Irreversible process: a process that, by a differential change in the environment, cannot be made to retrace its path. Note: irreversible processes cannot in general be represented graphically since some irreversible processes involve nonequilibrium states, which cannot be represented on a graph.

(c) State variable: a variable such that the integral over any closed path of the differential of that variable is zero, symbolically $\oint ds = 0$, where s is the symbol representing the state variable. Note: recall the definition of a conservative force in Conservation of Energy and note the similarity between this definition and the definition of a state variable. State variables that you have encountered in thermodynamics so far are: U (internal energy), p (pressure), T (temperature), and V (volume). Differential increments of variables that are not state variables will be represented by slashes through the ds , e.g., dQ and dW .

(d) Cycle: a sequence of processes that a system goes through, such that the system returns to its original equilibrium state. Note: cycles can be either reversible or irreversible.

(e) Efficiency: $e \equiv W_{\text{out}}/Q_{\text{in}}$ for a cycle.

(f) Carnot cycle: a cycle consisting of two reversible adiabatic processes and two reversible isothermal processes.

(g) Entropy: $dS \equiv dQ/T$, where S is the entropy, Q is the heat, and T is the absolute temperature. Note: The notation indicates that entropy is a state variable whereas heat (dQ) is not.

2. The Second Law of Thermodynamics

In your previous study of physics you have been concerned with conservation laws, i.e., conservation of energy (Conservation of Energy, Temperature, Heat, and Thermodynamics), conservation of linear momentum (Collisions), and conservation of angular momentum (Rotational Dynamics). Now we are going to consider a fundamental law of physics that is not a conservation law. In this case the law relates to a quantity that can never decrease when all parts of the interaction are considered. You already have considered a quantity that can proceed in one direction only, namely, time. You know from personal experience that people are born, age, and then die and not the other way around. This fundamental law we shall now study is necessary in order to understand why certain phenomena occur the way they do; for example, when we mix hot and cold water together the entire mixture comes to an equilibrium temperature somewhere in between the two initial temperatures. It never occurs (although according to statistical mechanics there is an infinitely small probability that it might) that the water that was initially hot gets hotter and the cold water gets colder. It would not violate the first law of thermodynamics (if the hot water did get hotter and the cold colder), thus we need another law to explain why this never happens. This law is simply called the "second law of thermodynamics" (indicating that physicists have very little

imagination). Your text gives several equivalent statements of the second law. The one that you should memorize (since it is more general and the other statements can be obtained from this statement) is

SECOND LAW OF THERMODYNAMICS

|| A process that starts in one equilibrium state and ends in another will proceed in the direction that causes the entropy of the system plus its environment to increase or to remain the same.

You will see that the second law of thermodynamics applied to reversible processes gives $\Delta S = 0$, and applied to irreversible processes gives $\Delta S > 0$. Since all real processes are irreversible, the second law should read something to the effect that for all real processes $\Delta S > 0$. However, since the analysis of reversible processes can yield much valuable information (like the analysis of projectile motion in the absence of perturbing effects like wind, etc.) we shall use the statement given above as our definition. Our analysis of the ramifications of the second law will for the most part (some of your texts briefly mention microscopic ramifications of the second law) be concerned with the macroscopic domain. For a more fundamental understanding of entropy and the second law, you are referred to the excellent text: Statistical Physics by Reif.*

3. Important Concepts

In addition to the second law of thermodynamics, the other important concepts in this module are

(a) Efficiency. Loosely speaking, the efficiency of a process is the measure of what we get out of the process divided by what we put into it. In thermodynamics we are concerned with heat engines (cycles involving an exchange of heat), and thus we define efficiency more precisely as given above in the definitions.

(b) The Carnot cycle. The Carnot cycle is important since the most efficient engine operating between two temperature reservoirs is that utilizing a Carnot cycle. The efficiency of the Carnot cycle is given by

$$e = 1 - T_c/T_h$$

and is independent of the working substance, e.g., an ideal gas or peanut butter. Since the efficiency is independent of the working substance we can define an absolute-temperature scale by use of the Carnot cycle. This temperature scale happens to be identical to the Kelvin scale introduced earlier in Temperature, Heat, and Thermodynamics. (This also shows that, whereas physicists may not be very imaginative, they do plan ahead.) Since they are easy to deal with, much of the material and many of the problems involve ideal gases; however, the concepts are general.

*X. X. Reif, Statistical Physics (McGraw-Hill, New York, 19XX), Berkeley Physics, Vol. V.

(c) Entropy. Entropy is a state variable of thermodynamic systems, and is involved in a fundamental law of thermodynamics, namely, the second law. It is also a measure of the disorder of a system; however, we shall not go into this aspect of it in the present module (see Reif* for elaboration).

(d) Adiabatic process. You need to know that for an ideal gas undergoing an adiabatic process, if $dQ = 0$, then

$$pV^\gamma = \text{const} \quad (\gamma = C_p/C_v).$$

TEXT: Frederick J. Bueche, Introduction to Physics for Scientists and Engineers (McGraw-Hill, New York, 1975), second edition

SUGGESTED STUDY PROCEDURE

Read Chapter 17, Section 17.4. Then, read sections 17.5 through 17.11. Notes: The sentence in the first paragraph of Section 17.5 beginning "Let us consider..." is misleading: Real engines cannot be represented on a pV diagram, since in real engines one does not have an equilibrium situation at any time during the operation. However, one can approximate the operation of a real engine by a well-chosen reversible cycle that can be represented on a pV diagram, and which then can be analyzed according to well-known thermodynamic procedures.

In Section 17.6, in the second paragraph the sentence, "When the system reaches point B it is suddenly (and therefore adiabatically) expanded along curve BC," is misleading. A sudden expansion is adiabatic by its very nature since there is no time for heat to be transferred. However, a Carnot cycle is a reversible cycle - a sudden expansion is an irreversible process and therefore cannot be part of a reversible cycle. The statement should be reformulated to read: "...it is expanded adiabatically - that is, slowly enough to be considered reversible yet quickly enough so that a significant amount of heat is not transferred to the gas from the environment. Both of these conditions can be satisfied by the use of sufficient insulation. Similar statements apply to the statement in the next paragraph dealing with an adiabatic compression. Equation (17.15) in Section 17.7 applies to a Carnot cycle independently of the working substance even though it was derived for an ideal gas. In the first full paragraph under Eq. (17.15) the sentence should read: "Although it applies only to the Carnot cycle, it nevertheless sets an upper limit for all other cycles, since they are less efficient than the Carnot cycle."

BUECHE

Objective Number	Readings	Problems with Solutions		Assigned Problems		Additional Problems (Chap. 17)
		Study Guide	Text	Study Guide (Chap. 17)	Text	
1	Secs. 17.2, 17.10, 17.6					
2	General Comments, Sec. 17.11					
3(a)	Secs. 17.5, 17.6	A		D	17	Quest. ^a 9 to 12
3(b)	Secs. 17.6, 17.7	B		E		Probs. 15, 18
3(c)	Secs. 17.10, 17.11	C	Illus. ^a 17.4, 17.5, Sec. 17.11, Cases 1, 2	F	19, 21	Probs. 20, 22, 23

^aIllus. = Illustration(s). Quest. = Question(s).

You should be able to show that the statement of the second law of thermodynamics given at the beginning of Section 17.8 (p. 311) follows from the statement given in the last sentence of Section 17.11 (on p. 320 prior to the Questions) and from our formulation in General Comment 2. Work Problems 17, 19, and 21 in Chapter 17 of your text and Problems A through F in this study guide. When you think you know the material well enough to satisfy the objectives, take the Practice Test.

TEXT: David Halliday and Robert Resnick, Fundamentals of Physics (Wiley, New York, 1970; revised printing, 1974)

SUGGESTED STUDY PROCEDURE

Read Example 5 in Section 21-6 (Chapter 20, pp. 385, 386). Then read Sections 21-1 through 21-8. Work Problems 1, 5, 7, 11, 16, 21, and 33 in Chapter and Problems A through F in this study guide. When you think that you know the material well enough to satisfy the objectives, take the Practice Test.

HALLIDAY AND RESNICK

Objective Number	Readings	Problems with Solutions		Assigned Problems		Additional Problems (Chap. 21)
		Study Guide (Chap. 21)	Text (Chap. 21)	Study Guide	Text (Chap. 21)	
1	General Comments, Secs. 21-2, 21-2, 21-6, 21-3					Quest. ^a 4, 7, 2, 5, 6, 10, 11, 18
2	General Comments, Secs. 21-1, 21-8					Quest. 3
3(a)	Secs. 21-3, 21-5	A		D	11, 16	Probs. 10, 14, 17, 18, 19
3(b)	Sec. 21-3	B	Ex. ^a 1, 2	E	1, 5, 7	Quest. 8, 9, 12, Probs. 2, 3, 8
3(c)	Secs. 21-6, 21-7, 21-8	C	Ex. 3, 4	F	21, 33	Quest. 14 to 17, Probs. 20, 23, 25 to 32

^aEx. = Example(s). Quest. = Question(s).

TEXT: Francis Weston Sears and Mark W. Zemansky, University Physics (Addison-Wesley, Reading, Mass., 1970), fourth edition

SUGGESTED STUDY PROCEDURE

Read Section 19-13 in Chapter 19. Then read Sections 19-14 through 19-24. Note: Your text does not distinguish between state variables and nonstate variables. Make sure you understand this distinction from the material in General Comment 1. When you think that you do, write the first law of thermodynamics in differential form, distinguishing state variables from nonstate variables. (See answer at the bottom of this page.) If you missed this, review the material again - if you still do not understand this, ask your tutor for assistance.

You should be able to show that the statements of the second law of thermodynamics given in Sections 19-18 and 19-19 (pp. 274, 276) of the text follow from the statement given in Section 19-24 (p. 280) and General Comment 2. Work Problems 19-24, 19-26, 19-31, 19-32 in your text, and Problems A through F in this study guide. When you think that you know the material well enough to satisfy the objectives, take the Practice Test.

SEARS AND ZEMANSKY

Objective Number	Readings	Problems with Solutions		Assigned Problems		Additional Problems
		Study Guide	Text	Study Guide	Text	
1	General Comments, Secs. 19-20, 19-14, 19-23					
2	General Comments, Sec. 19-24					
3(a)	Secs. 19-14 to 19-17, 19-19, 19-20	A		D	19-24	19-23, 19-25, 19-30
3(b)	Secs. 19-20 to 19-22	B		E	19-26	19-27 to 19-29
3(c)	Secs. 19-23, 19-24	C	Ex. ^a 1, 2, 3 (Sec. 19-23)	F	19-31, 19-32	

^aEx. = Example(s).

TEXT: Richard T. Weidner and Robert L. Sells, Elementary Classical Physics (Allyn and Bacon, Boston, 1973), second edition, Vol. 1

SUGGESTED STUDY PROCEDURE

Read Chapter 18, Section 18-6, and Chapter 21, Sections 21-1 through 21-6.
Notes: Your text does not define the concept of state variable explicitly but, rather, alludes to it in the discussion of Eq. (19-13) (pp. 428, 429). Study the definition given in General Comment 1. When you think that you understand this definition, write the first law of thermodynamics in differential form, distinguishing state variables from nonstate variables. (See answer at the bottom of this page.) If you missed this, review the material again - if you still do not understand this, ask your tutor for assistance.

In Section 21-2, on p. 430, the sentence beginning "Chemical or nuclear potential energy..." is misleading. Although it is theoretically possible to convert chemical or nuclear potential energy into thermal energy with 100% efficiency, the author of this module is unaware of any practical device that does so. Work Problems 21-5, 21-6, 21-9, 21-11 in your text and Problems A through F in this study guide. When you think that you know the material well enough to satisfy the objectives, take the Practice Test.

WEIDNER AND SELLS

Objective Number	Readings	Problems with Solutions		Assigned Problems		Additional Problems
		Study Guide	Text	Study Guide	Text	
1	General Comments, Secs. 21-1, 18-6, 21-2, 21-4, 21-5					
2	General Comments, Sec. 21-6					
3(a)	Secs. 21-1, 21-2	A	Ex. ^a 21-1	D	21-5	21-2, 21-4
3(b)	Secs. 21-3, 21-4	B	Ex. 21-2	E	21-6	21-7, 21-8
3(c)	Secs. 21-5, 21-6	C	Ex. 21-4, 21-5, 21-6	F	21-9, 21-11	21-10, 21-12, 21-13, 21-14

^aEx. = Example(s).

PROBLEM SET WITH SOLUTIONS

A(3). The gas in the internal combustion engine in your car undergoes a process that can be approximated by a cycle called the Otto cycle. The Otto cycle consists of (1) an adiabatic compression from V_1 to V_2 , (2) a pressure increase at constant volume V_2 , (3) an adiabatic expansion from V_2 to V_1 , and (4) a pressure decrease at constant volume V_1 back to the original pressure.

- (a) Why can we not analyze the real process that the gas undergoes in an internal combustion engine?
 (b) Draw the Otto cycle on a pV diagram.
 (c) Assuming that the gas is an ideal gas, show that the efficiency of the Otto cycle is

$$e = 1 - (V_2/V_1)^{\gamma - 1}$$

where $\gamma \equiv C_p/C_v$. For an ideal gas, $C_p = C_v + R$.

- (d) What is the efficiency of an engine whose compression ratio V_1/V_2 is 10 and whose $\gamma = 1.40$?

Solution

(a) The gases in real engines undergo irreversible processes that cannot be plotted on a pV diagram, since the gases are never in an equilibrium state (and only equilibrium states can be represented on a pV diagram).

(b) See Figure 1.

(c) $e = W/Q_{in}$. Since work is done only during the adiabatic processes, let us find an expression for work for an ideal gas during an adiabatic process:

$$\begin{aligned} dW &= p \, dV, & pV^\gamma &= C = p_i V_i^\gamma, \\ W &= \int_{V_i}^{V_f} \frac{C}{V^\gamma} \, dV = c \left(\frac{1}{1-\gamma} \right) V^{1-\gamma} \Big|_{V_i}^{V_f} = \left(\frac{c}{1-\gamma} \right) [V_f^{1-\gamma} - V_i^{1-\gamma}] \\ &= \frac{p_i V_i^\gamma}{1-\gamma} [V_f^{1-\gamma} - V_i^{1-\gamma}]. \end{aligned} \quad (1)$$

Now the only time heat enters or leaves the gas is during the constant-volume process: $dQ = nC_v \, dT$. Q_{in} occurs during process $b \rightarrow c$. Since p is increasing as V remains constant, T increases, or heat is added to system:

$$Q_{in} = nC_v(T_f - T_i). \quad (2)$$

Now let us calculate the total work. Using Equation (1), we have

$$W = W_{cd} + W_{ab} = [p_c V_2^\gamma / (1 - \gamma)] (V_1^{1-\gamma} - V_2^{1-\gamma}) + [p_a V_1^\gamma / (1 - \gamma)] (V_2^{1-\gamma} - V_1^{1-\gamma}).$$

Now $Q_{in} = nC_v(T_c - T_b)$, thus

$$e = \frac{p_c V_2^\gamma (V_1^{1-\gamma} - V_2^{1-\gamma}) + p_a V_1^\gamma (V_2^{1-\gamma} - V_1^{1-\gamma})}{(1 - \gamma)nC_v(T_c - T_b)}$$

$$= \frac{p_c V_2 [(V_1^{1-\gamma}/V_2) - 1] + p_a V_1 [(V_2/V_1)^{1-\gamma} - 1]}{(1 - \gamma)nC_v(T_c - T_b)}, \quad \text{where } V_2/V_1 \equiv \alpha.$$

$$e = \frac{nRT_c(\alpha^\gamma - 1) + nRT_a(\alpha^{1-\gamma} - 1)}{(1 - \gamma)nC_v(T_c - T_b)}.$$

Now use the fact that $C_p = C_v + R$ for ideal gases to eliminate R:

$$\frac{T_c(\alpha^\gamma - 1) + T_a(\alpha^{1-\gamma} - 1)}{(1 - \gamma)[C_v/(C_p - C_v)](T_c - T_b)} = \frac{T_c(\alpha^\gamma - 1) + T_a(\alpha^{1-\gamma} - 1)}{T_b - T_c}.$$

Since $p_a V_1^\gamma = p_b V_2^\gamma$,

$$p_a V_1 (V_1^\gamma - 1) = p_b V_2 (V_2^\gamma - 1), \quad nRT_a (V_1^\gamma - 1) = nRT_b (V_2^\gamma - 1),$$

or

$$T_a V_1^{\gamma-1} = T_b V_2^{\gamma-1} \quad \text{and} \quad T_a = T_b \alpha^{\gamma-1}.$$

Thus

$$e = \frac{T_c(\alpha^\gamma - 1) + T_b \alpha^{\gamma-1}(\alpha^{1-\gamma} - 1)}{T_b - T_c} = \frac{T_c(\alpha^\gamma - 1) + T_b(1 - \alpha^{\gamma-1})}{T_b - T_c}$$

$$= 1 - \alpha^{\gamma-1}.$$

Or $e = 1 - (V_2/V_1)^{\gamma-1}$

$$(d) e = 1.00 - (0.100)^{0.40} = 1.00 - 0.40 = 0.60.$$

- B(3). A Carnot engine is operated as a refrigerator. If the high-temperature reservoir is at 300 K and the low-temperature reservoir is at 270 K, find the amount of heat that can be removed from the low-temperature reservoir in 10.0 min if the power input is 200 w.

Figure 1

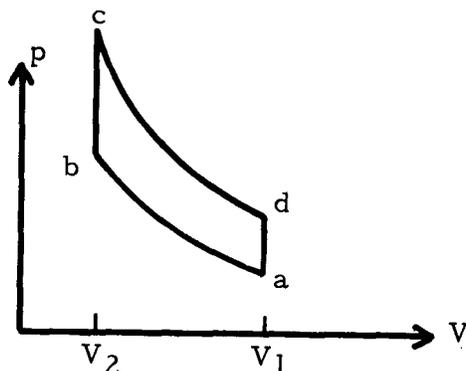
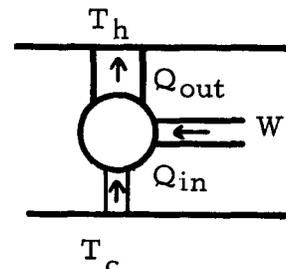


Figure 2

Solution

See Figure 2. We are given that $P = 200 \text{ w}$, $T_c = 270 \text{ K}$, and $T_h = 300 \text{ K}$. We are to find $Q_{in} = ??$ in 10.0 min.

$$e = 1 - \frac{T_c}{T_h} = \frac{W}{Q_{out}}, \quad Q_{out} = W + Q_{in}, \quad 1 - \frac{T_c}{T_h} = \frac{W}{(W + Q_{in})},$$

$$W + Q_{in} = \frac{T_h W}{T_h - T_c}, \quad Q_{in} = W \left(\frac{T_h}{T_h - T_c} \right) - 1 = W \left(\frac{T_h - T_h + T_c}{T_h - T_c} \right) = W \left(\frac{T_c}{T_h - T_c} \right),$$

$$dQ_{in}/dt = (dW/dt) [T_c/T_h - T_c], \quad P \equiv dW/dt.$$

$$dQ_{in}/dt = (200 \text{ w}) [270 \text{ K} / (300 \text{ K} - 270 \text{ K})] = (200 \text{ w}) 9.0 = 1800 \text{ w}.$$

$$Q_{in} = \int \frac{dQ_{in}}{dt} dt = \int_0^{10.0 \text{ min}} (1800 \text{ w}) dt = (1800 \text{ w}) \int_0^{10.0 \text{ min}} dt$$

$$= (1800 \text{ w}) t \Big|_0^{10.0 \text{ min}} = (1800 \text{ w})(10.0 \text{ min})(60 \text{ s}/1 \text{ min}),$$

$$Q = 1.80(10^3)(10)(6.0)(10) \text{ w} = 1.10(10^6) \text{ J} - \text{reasonable??}$$

- C(3). (a) A mass m (specific heat C) is heated from T_1 to T_2 . Show that the entropy change is given by $\Delta S = mc \ln(T_2/T_1)$.
 (b) Does the entropy of this substance decrease on cooling? If it does, explain how this can happen in light of the second law of thermodynamics.

Solution

Given M , C , $T_i = T_1$, and $T_f = T_2$, we are (a) to show that $S_2 - S_1 = mc \ln(T_2/T_1)$; and (b) show if $\delta Q < 0$ whether $dS < 0$, and if so, show how this occurs in light of the second law.

$$(a) \delta Q = mC dT, \quad dS = \delta Q/T, \quad dS = mC dT/T,$$

$$\int_{S_2}^{S_1} dS = mC \int_{T_1}^{T_2} (dT/T), \quad S_2 - S_1 = mC \ln \left| \frac{T_2}{T_1} \right|,$$

$S_2 - S_1 = mC \ln(T_2/T_1)$ dimensions?? Is the answer reasonable? How does it depend on m ? C ? T_2 ? T_1 ?

(b) On cooling $T_2 < T_1$,

$$\ln(T_2/T_1) < 0, \quad S_2 - S_1 < 0.$$

The total entropy will remain unchanged if the process is reversible, since the entropy of the environment will increase by just the right amount to maintain the entropy at a constant value. If the process is irreversible then

$$|ds_{\text{environment}}| > |ds_{\text{substances}}|.$$

The total entropy will increase.

Problems

- D(3). One mole of an ideal gas passes through the cycle shown on the pV diagram in Figure 3. All answers are to be expressed in terms of p_1 , V_1 , T_1 , and R . $\gamma = 5/3$.
 (a) Find p_2 . (b) Find p_3 and T_3 . What is the net work done in one cycle?

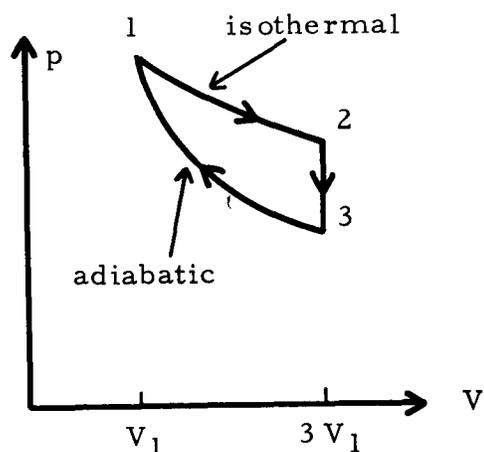


Figure 3

- E(3). (a) A Carnot engine operates with a hot reservoir at 400 K. If this engine has an efficiency of 30%, what is the temperature of the cold reservoir?
 (b) A real steam engine operates with the same cold reservoir as in part (a) with the same efficiency; what do you know about its hot reservoir?
- F(3). One end of a cylindrical rod is thermally in contact with a heat reservoir whose temperature is 127°C; the other end is thermally in contact with a heat reservoir whose temperature is 27°C. After the rod has achieved steady-state conditions: (a) Compute the change in the entropy of the universe due to 5021 J of heat flowing through the rod. (b) Does the entropy of the rod change during this process? Why or why not?

Solutions

- D(3). (a) Use $T_1 = T_2$ to find $p_2 = p_1/3$.
 (b) Use $V_2 = V_3$ and $p_3 V_3^\gamma = p_1 V_1^\gamma$ to find $p_3 = 0.160p_1$ and $T_3 = 0.48T_1$.
 (c) Use $W = \int p \, dW$ to find $W = 0.320RT_1$.
- E(3). (a) $e = 1 - T_c/T_h$, $T_c = 280$ K.
 (b) $e_{\text{Carnot}} \geq e_{\text{any other device operating between the same two temperature reservoirs}}$
 $T_h(\text{steam}) \geq T_h(\text{Carnot})$.
- F(3). (a) $\Delta S_{\text{total}} = 4.2$ J/K.
 (b) No, the rod does not change its state. Since S is a state variable, $\Delta S_{\text{rod}} = 0$.

PRACTICE TEST

- Define: (a) state variable, (b) efficiency, and (3) entropy.
- State the second law of thermodynamics as it relates to entropy on a macroscopic scale, and show that the second-law statements relating to heat flow satisfy this statement.
- (a) A Carnot-cycle heat engine operates between a thermal reservoir at a temperature of 140°C and a reservoir at 40°C. If the engine does 2092 J of work, calculate the heat taken in and the heat rejected.
 (b) Calculate the change in entropy of the engine for each process of the Carnot cycle in part (a), and then calculate the total entropy change for the cycle.

Practice Test Answers

1. (a) A variable such that the integral over any closed path of the differential of the state variable is zero, symbolically $\oint dS = 0$.
 (b) $e \equiv W_{\text{out}}/Q_{\text{in}}$ over a cycle.
 (c) $dS \equiv \delta Q/T$, where S is the entropy, Q heat, and T the absolute temperature.
2. A process that starts in one equilibrium state and ends in another will go in the direction that causes the entropy of the system plus its environment to increase or to remain the same.

One of the second-law statements relating to heat flow is: "There can be no process whose sole effect is to convert a given amount of heat energy into work." Applying the second-law statement relating to entropy to an engine whose only effect is to convert heat into work we have $\Delta S < 0$, since an amount of heat is taken from the heat reservoir. This violates the entropy statement of our second law; therefore, the above process is impossible.

The other second-law statement relating to heat flow is "There can be no process whose sole effect is to transfer an amount of heat from a low-temperature reservoir to a high-temperature reservoir." Applying the second-law statement relating to entropy to an engine whose only effect is to transfer heat from a low-temperature reservoir to a high-temperature reservoir we have

$$S = -\frac{Q}{T_c} + \frac{Q}{T_h} = Q\left(\frac{1}{T_h} - \frac{1}{T_c}\right).$$

Now $1/T_h < 1/T_c$; therefore $\Delta S < 0$, which violates the entropy statement of the second law. Thus this process is also impossible.

3. (a) $e = \frac{W_{\text{out}}}{Q_{\text{in}}} = 1 - \frac{T_c}{T_h}$ for a Carnot cycle.

$$Q_{\text{in}} = \frac{W_{\text{out}}}{1 - T_c/T_h} = \frac{2092 \text{ J}}{1 - (313 \text{ K})/(413 \text{ K})} = 8.7 \times 10^3 \text{ J},$$

$$Q_{\text{out}} = Q_{\text{in}} - W_{\text{out}} = 6.6 \times 10^3 \text{ J}.$$

- (b) $dS \equiv \delta Q/T$. For two adiabatic parts of cycle $\delta Q = 0$, $\Delta S = 0$. For a high-temperature isothermal process: T constant,

$$\Delta S = \Delta Q/T = (8.7 \times 10^3 \text{ J})/(413 \text{ K}) = 21.1 \text{ J/K}.$$

For a low-temperature isothermal process: T constant,

$$\Delta S = (-6.6 \times 10^3 \text{ J}) / (313 \text{ K}) = -21.1 \text{ J/K}, \quad \Delta S_{\text{total}} = 0.$$

This is reasonable since the Carnot cycle is a reversible cycle and $\Delta S = 0$ for reversible cycles.

If you got 100% on this Practice Test, ask for a Mastery Test; if not, study the relevant material, work some more of the Additional Problems, and when you think that you understand that material ask for a Mastery Test.

SECOND LAW AND ENTROPY

Date _____

Mastery Test Form A

pass recycle

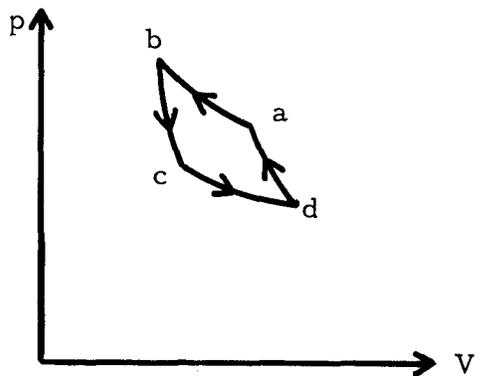
1 2 3

Name _____

Tutor _____

1. Define (a) state variable, (b) cycle, and (c) entropy.
2. State the second law of thermodynamics as it relates to entropy on a macroscopic scale, and show that the second-law statements relating to heat flow satisfy this statement.
3. Four moles of an ideal gas is caused to expand from a volume V_1 to a volume $V_2 (= 2V_1)$.
 - (a) If the expansion is isothermal at the temperature $T = 400$ K, deduce an expression for the work done by the expanding gas.
 - (b) For the isothermal expansion just described, deduce an expression for the change in entropy, if any.
 - (c) If the expansion were reversibly adiabatic instead of isothermal, would the change in entropy of the gas be positive, negative, or zero?
4. A pV diagram of a Carnot cycle is sketched in Figure 1.
 - (a) Is the device operating as an engine or a refrigerator?
 - (b) In which part(s) of the cycle does heat flow into this device? Out of it?
 - (c) In which part(s) of the cycle does the temperature of the working substance increase? Decrease?
 - (d) Does the entropy of the working substance decrease in any part of this cycle? If not, prove that it cannot; if so, indicate in which part of the cycle.

Figure 1



SECOND LAW AND ENTROPY

Date _____

Mastery Test Form B

pass recycle

1 2 3

Name _____ Tutor _____

1. Define (a) irreversible process, (b) efficiency, and (c) Carnot cycle.
2. State the second law of thermodynamics as it relates to entropy on a macroscopic scale, and show that the second-law statements relating to heat flow satisfy this statement.
3. A Carnot refrigerator takes heat from water at 0°C and discards heat to the room at a temperature of 27°C . If 100 kg of water is frozen to ice at 0°C by this refrigerator (the latent heat of fusion is 335 J/g).
 - (a) How many joules are discarded to the room?
 - (b) What is the required work?
4. One mole (63.5 g) of copper at 100°C is placed in a block of ice and remains until the whole comes to thermal equilibrium at 0°C . The latent heat of fusion (the amount of heat necessary to convert 1.00 g of ice to 1.00 g of water at 0°C) of ice is 33 J/g . The specific heat of copper is 25.1 J/mol K .
 - (a) How much water is formed?
 - (b) What is the entropy change of the copper?
 - (c) What is the entropy change of the water?
 - (d) What is the total entropy change of the system?

SECOND LAW AND ENTROPY

Date _____

Mastery Test Form C

pass recycle

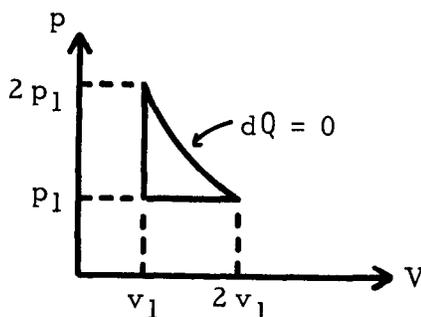
1 2 3

Name _____

Tutor _____

1. Define (a) state variable, (b) cycle, and (c) entropy.
2. State the second law of thermodynamics as it relates to entropy on a macroscopic scale, and show that the second-law statements relating to heat flow satisfy this statement.
3. (a) Calculate the efficiency of an engine using an ideal gas taken around the cycle shown in Figure 1, where $\gamma = 5/3$. For an ideal gas, $C_p = C_v + R$.
 (b) Draw a Carnot cycle on a temperature-entropy (TS) diagram. Work is just the area enclosed by the curve representing a cycle on a pV plot. Can a similar interpretation be made regarding a TS plot?

Figure 1



SECOND LAW AND ENTROPY

Date _____

Mastery Test Form D

pass recycle

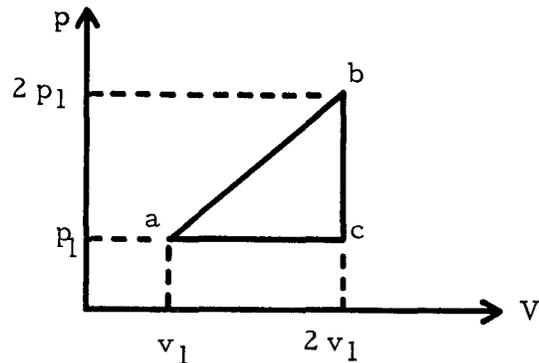
1 2 3

Name _____

Tutor _____

1. Define (a) irreversible process, (b) efficiency, and (c) entropy.
2. State the second law of thermodynamics as it relates to entropy on a macroscopic scale, and show that the second-law statements relating to heat flow satisfy this statement.
3. (a) Calculate the efficiency of an engine using an ideal gas taken around the cycle in Figure 1, where $U = (3/2)RT$, $C_v = (3/2)R$ and $C_p = (5/2)R$ for this gas.
 (b) In a specific-heat experiment 100 g of lead ($C_p = 0.144 \text{ J/g K}$) at 100°C is mixed with 200 g of water at 20°C . Find the difference in entropy of the system at the end from its value before mixing.

Figure 1



SECOND LAW AND ENTROPY

Date _____

Mastery Test Form E

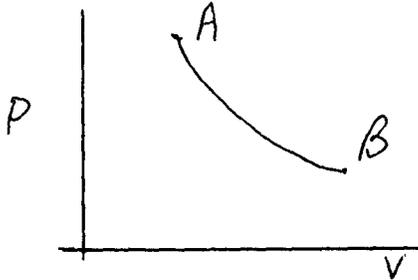
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1 2 3

Name _____

Tutor _____

1.



The curve AB represents an isothermal process i.e. $PV = \text{constant}$. If one has two moles of an ideal monatomic gas at A under pressure of $2.5 \times 10^5 \text{ N/m}^2$ volume of $20 \times 10^{-3} \text{ m}^3$, and temperature 300°K and it goes to B where the pressure is 10^5 N/m^2 , (Given $C_v = 3 \text{ cal/mol}^\circ\text{C}$, and $\gamma = 5/3$), what is the entropy change in going from A to B? What condition

must exist for the process to be reversible?

2. Two moles of an ideal gas initially at a pressure of 4 atmospheres, volume of 12.3 liters and temperature of 300°K undergo the following cycle; (1) heat at constant volume to a pressure of 5 atmospheres (2) heated at constant pressure to a temperature of 500°K (3) cooled at constant volume to a pressure of 4 atmospheres (4) cooled at constant pressure to the original volume. Sketch cycle.

Given: $R = 0.082 \text{ liter} \cdot \text{atmospheres per mol per degree Kelvin}$; $R = 1.99 \text{ cal/mol}^\circ\text{K}$; $C_p = 7 \text{ cal/mol}^\circ\text{K}$, $C_v = 5 \text{ cal/mol}^\circ\text{K}$; $1 \text{ cal} = 4.2 \text{ joules}$).

Find a) Find the heat added or rejected, the work done on or by the gas, and the change in internal energy for each of 4 steps given above.

b) What was the total work done during the cycle?

c) What would be the efficiency of an engine using this cycle? How would this efficiency compare with that of a Carnot Engine operating in the same temperature range?

SECOND LAW AND ENTROPY

Date _____

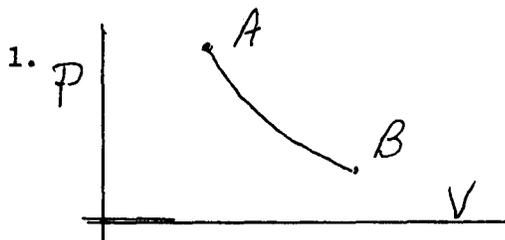
Mastery Test Form F

pass recycle

1 2 3

Name _____

Tutor _____



The curve AB represents an adiabatic process. i.e. $PV^\gamma = \text{constant}$. If one has two moles of an ideal gas at A under pressure of $2.5 \times 10^5 \text{ N/m}^2$ with a volume $20 \times 10^{-3} \text{ m}^3$ and a temperature of 300°K and it expands to B where the pressure is 10^5 N/m^2 ,

what is the entropy change in going from A to B? Given $C_v = 3 \text{ cal/mol } ^\circ\text{C}$ and $\gamma = 5/3$. Is the process reversible? What does it mean to you?

2. An ideal gas initially at a pressure of 3 atmospheres, a volume of 2.46 liters, and a temperature of 300°K undergoes the following cycle; (a) heated at constant volume to a pressure of 4 atmospheres; (b) heated at constant pressure to a temperature of 600°K ; (c) cooled at constant volume to its original pressure, and (d) cooled at constant pressure to its original volume. Sketch cycle. (a) Find the mass of the gas in moles. (b) Find the heat added or rejected, the work done on or by the gas, and the change in the internal energy for each of the changes. (c) Find the efficiency of an engine utilizing this cycle. ($R = 0.082 \text{ liter-atmospheres per mole per degree Kelvin}$; $C_p = 7 \text{ cal/mol-}^\circ\text{K}$, $C_v = 5 \text{ cal/mol-}^\circ\text{K}$; $1 \text{ Cal} = 4.2 \text{ joules}$.)

MASTERY TEST GRADING KEY - Form A

1. What To Look For: (a) $\oint dS = 0$. (c) Absolute temperature.

Solution: (a) A variable such that the integral over any closed path of the differential of the state variable is zero, symbolically $\oint dS = 0$.

(b) A sequence of processes that a system goes through such that the system returns to its original equilibrium state.

(c) $dS \equiv \delta Q/T$, where S is the entropy, Q is the heat, and T is the absolute temperature.

2. What To Look For: $\Delta S_{\text{universe}} \geq 0$.

Solution: A process that starts in one equilibrium state and ends in another will go in the direction that causes the entropy of the system plus its environment to increase or to remain the same.

One of the second-law statements relating to heat flow is: "There can be no process whose sole effect is to convert a given amount of heat energy into work." Applying the second-law statement relating to entropy to an engine whose only effect is to convert heat into work we have $\Delta S < 0$, since an amount of heat is taken from the heat reservoir. This violates the entropy statement of our second law; therefore, the above process is impossible.

The other second-law statement relating to heat flow is "There can be no process whose sole effect is to transfer an amount of heat from a low-temperature reservoir to a high-temperature reservoir." Applying the second-law statement relating to entropy to an engine whose only effect is to transfer heat from a low-temperature reservoir to a high-temperature reservoir we have

$$\Delta S = -\frac{Q}{T_c} + \frac{Q}{T_h} = Q\left(\frac{1}{T_h} - \frac{1}{T_c}\right).$$

Now $1/T_h < 1/T_c$; therefore $\Delta S < 0$, which violates the entropy statement of the second law. Thus this process is also impossible.

3. What To Look For: (a) $W = \int p \, dV$, $pV = nRT$. (b) Use of first law to deduce expression for entropy. (c) $dS = \delta Q/T$, $\delta Q = 0$.

Solution: (a) $n = 4.0 \text{ mol}$, $pV = nRT$.

$$W = \int_{V_i}^{V_f} \frac{nRT}{V} \, dV = nRT \ln\left(\frac{V_f}{V_i}\right) = 3200 \ln(8.4 \text{ J}).$$

(b) $dU = 0$ since $U = U(T)$ for an ideal gas. $\delta Q = \delta W$, $dS = \frac{\delta W}{T}$, or

$$\Delta S = \int \frac{dW}{T} = \frac{1}{T} \int dW = 8 \ln(8.4 \text{ J/K}).$$

(c) $\Delta S = 0.$

4. What To Look For: (a) Use the fact that the Carnot cycle is independent of working substance. Now use an ideal gas as working substance. Recognize which are isothermal and which are adiabatic. Utilize first law and the fact that $U = U(T)$ for an ideal gas to deduce sign of dQ .
 (b) Same as part (a).
 (c) Utilize $pV = nRT$ to deduce regions where $\Delta T > 0$ and $\Delta T < 0$.
 (d) $dS \equiv dQ/T$. If $dQ = 0$, $\Delta S = 0$. If $dQ < 0$, $\Delta S < 0$. If $dQ > 0$, $\Delta S > 0$.

Solution: (a) In a refrigerator, $a \rightarrow b$ high-temperature compression, $dU = 0$; therefore $dQ = dW$, $dW_{a \rightarrow b} < 0$; therefore $dQ < 0$.

Heat leaves system at the high-temperature reservoir, therefore this is a refrigerator.

(b) $c \rightarrow d$ is Q_{in} , $a \rightarrow b$ is Q_{out} .

(c) $d \rightarrow a$ is $\Delta T > 0$, $b \rightarrow c$ is $\Delta T < 0$.

(d) Yes, $a \rightarrow b$.

MASTERY TEST GRADING KEY - Form B

1. Solution: (a) A process that, by a differential change in the environment cannot be made to retrace its path.
 (b) $e \equiv W_{\text{out}}/Q_{\text{in}}$ for a cycle.
 (c) A cycle consisting of two adiabatic processes and two isothermal processes.

2. What To Look For: $\Delta S_{\text{universe}} \geq 0$.

Solution: See solution to Problem 2 in Mastery Test Grading Key - Form A.

3. What To Look For: (a) Recognize that a Carnot cycle is a reversible cycle.
 $Q_c/Q_h = T_c/T_h$ for Carnot cycle. $Q = mL$.
 (b) $W = Q_h - Q_c$.

Solution: (a) $Q_c = (10^5 \text{ g})(335 \text{ J/g}) = 34 \times 10^6 \text{ J}$.

$$Q_h = (T_h/T_c)Q_c = (300/273)(34 \times 10^6 \text{ J}) = 34 \times 10^6 \text{ J}$$

This is reasonable since $Q_h > Q_c$.

(b) $W = 3.3 \times 10^6 \text{ J}$.

4. What To Look For: (a) Energy conserved.
 (b) $dS \equiv \delta Q/T$.
 (c) $dS \equiv \delta Q/T$.

Solution: (a) $mL = m_{\text{Cu}} C_{\text{Cu}} \Delta T_{\text{Cu}}$,

$$m = \frac{(100 \text{ mol})(25.1 \text{ J/mol K})(100 \text{ K})}{335 \text{ J/g}} = 7.5 \text{ g}$$

(b) $\Delta S_{\text{Cu}} = mc \int (dT/T) = (25.1 \text{ J/K}) \ln(273/373) = -7.9 \text{ J/K}$.

(c) $\Delta S_{\text{water}} = mL/T = (7.5 \text{ g})(335 \text{ J})/(273 \text{ K g}) = 9.2 \text{ J/K}$.

(d) $\Delta S_{\text{total}} \approx 1.26 \text{ J/K}$.

MASTERY TEST GRADING KEY - Form C

1. What To Look For: (a) $\oint dS = 0$. (c) $T =$ absolute temperature.

Solution: (a) A variable such that the integral over any closed path of the differential of the state variable is zero, symbolically $\oint dS = 0$.
 (b) A sequence of processes that a system goes through such that the system returns to its original equilibrium state.
 (c) $dS \equiv \delta Q/T$, where S is the entropy, Q the heat, and T the absolute temperature.

2. What To Look For: $\Delta S_{\text{universe}} \geq 0$.

Solution: See solution to Problem 2 in Mastery Test Grading Key - Form A.

3. What To Look For: $e = W/Q_{\text{in}}$, $\Delta Q = nC_V \Delta T$, $\Delta Q = nC_p \Delta T$. $W = \int p dV$.
 $\Delta Q = 0$, $pV^\gamma = \text{const}$ for ideal gas. $pV = nRT$ for ideal gas.
 (b) Recognize definition of Carnot cycle two $\Delta Q = 0$ and two $\Delta T = 0$ processes.
 $dS \equiv \delta Q/T$.

Solution: (a) For the work done by the adiabatic process:

$$W_{\text{done by}} = \int p dV = C \int_{V_i}^{V_f} \frac{dV}{V^\gamma} = C \frac{1}{1-\gamma} V^{1-\gamma} \Big|_{V_i}^{V_f} = \frac{2p_1 V_1^{5/3}}{-(2/3)} [(2V_1)^{-2/3} - (V_1)^{-2/3}]$$

$$= -3p_1 V_1 [2^{-2/3} - 1] = 3p_1 V_1 [1 - 2^{-2/3}] = 1.10 p_1 V_1.$$

$$W_{\text{done on}} = p_1 V_1.$$

$$\text{Therefore, } W_{\text{total}} = 0.10 p_1 V_1.$$

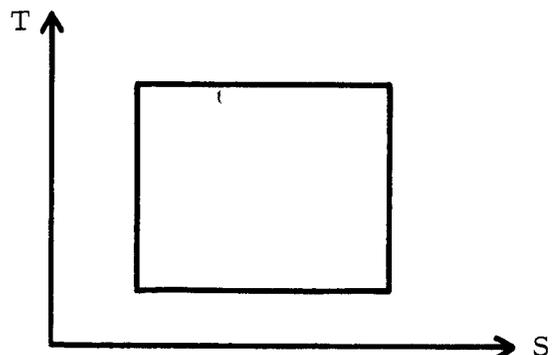
$$Q_{\text{in}} = nC_V \Delta T, \quad T_f = 2p_1 V_1/nR, \quad T_i = p_1 V_1/nR.$$

$$\text{Therefore } Q_{\text{in}} = nC_V (p_1 V_1/nR) = p_1 V_1/(\gamma - 1) = (3/2)p_1 V_1.$$

$$\text{Therefore } e = 0.067.$$

- (b) See Figure 7. Area = $\int T dS$. $\delta Q = T dS$. Therefore, $\Delta Q =$ area on TS plot.

Figure 7



MASTERY TEST GRADING KEY - Form D

1. What To Look For: (c) T = absolute temperature.

Solution: (a) A process that by a differential change in the environment cannot be made to return to its path.

(b) $e = W_{\text{out}}/Q_{\text{in}}$ for a cycle.

(c) $dS \equiv \delta Q/T$, where S is the entropy, Q is the heat, and T the absolute temperature.

2. What To Look For: $\Delta S_{\text{universe}} \geq 0$.

Solution: See solution to Problem 2 in Mastery Test Grading Key - Form A.

3. What To Look For: (a) $e = W/Q_{\text{in}}$. $W = \int p \, dV$. Calculate heat on straight part by using first law and ΔW . $\Delta Q = nC_V \Delta T$, $\Delta Q = nC_p \Delta T$, $pV = nRT$.

(b) $dS \equiv \delta Q/T$. $\delta Q = nc \, dT$. Conservation of energy.

Solution: (a) By inspection of the figure, we see that

$$W_{\text{total}} = (1/2)p_1V_1, \quad Q_{\text{ab}} = U_{\text{ab}} + W_{\text{ab}}.$$

$$W_{\text{ab}} = (3/2)p_1V_1, \quad U_{\text{ab}} = (3/2)R(T_b - T_a),$$

$$T_a = p_1V_1/nR, \quad T_b = 4p_1V_1/nR, \quad U_{\text{ab}} = (3/2)R(3p_1V_1/nR) = 9p_1V_1/2,$$

$$Q_{\text{ab}} = 9p_1V_1/2 + (3/2)p_1V_1 = 6p_1V_1 \text{ (it's positive)}$$

Q_{ab} is part of Q_{in} .

$$Q_{\text{bc}}: \Delta T < 0, \quad \text{therefore } Q_{\text{bc}} < 0,$$

$$Q_{\text{ca}}: \Delta T < 0, \quad \text{therefore } Q_{\text{ca}} < 0.$$

Or

$$e = (1/2)(p_1V_1/6p_1V_1) = 1/12.$$

(b) $dS \equiv \delta Q/T = mc(dT/T)$. Therefore $\Delta S = mc \ln(T_f/T_i)$.

$$\Delta S_{\text{sys}} = \Delta S_{\text{Pb}} + \Delta S_{\text{W}}, \quad m_{\text{Pb}}C_{\text{Pb}} \Delta T_{\text{Pb}} = m_{\text{W}}c_{\text{W}} \Delta T_{\text{W}}, \quad m_{\text{Pb}}C_{\text{Pb}}(T_{\text{Pb}_i} - T) = m_{\text{W}}c_{\text{W}}(T - T_{\text{W}_i}),$$

$$T = \frac{m_{\text{Pb}} C_{\text{Pb}} T_{\text{Pb}_i} + m_{\text{W}} C_{\text{W}} T_{\text{W}_i}}{m_{\text{Pb}} C_{\text{Pb}} + m_{\text{W}} C_{\text{W}}}$$
$$= \frac{(100 \text{ g})(14.4 \times 10^{-2} \text{ J/g}^\circ\text{C})(100^\circ\text{C}) + (200 \text{ g})(4.18 \text{ J/g}^\circ\text{C})(20^\circ\text{C})}{14.4 \text{ J/}^\circ\text{C} + 836 \text{ J/}^\circ\text{C}} = 21.4^\circ\text{C}.$$

$$\Delta S_{\text{Pb}} = (14.4 \text{ J/}^\circ\text{C}) \ln(294/373) = -3.4 \text{ J/}^\circ\text{C},$$

$$\Delta S_{\text{W}} = (836 \text{ J/}^\circ\text{C}) \ln(294.4/293.0) = 4.0 \text{ J/}^\circ\text{C}.$$

$$\text{Therefore } S_{\text{total}} = 0.60 \text{ J/}^\circ\text{C}.$$
