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Title: Entropy

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Input Skills:

- 1. Skills from "The First Law of Thermodynamics," (MISN-0-158).
- 2. Skills from "Energy Distribution Functions: Boltzmann Distribution," (MISN-0-159).

Output Skills (Problem Solving):

- S1. Write down the expression that defines the entropy change of a system for a reversible process, defining the terms in the expression.
- S2. Starting from the expression obtained in S1, above, determine the entropy change for a system that undergoes a reversible isothermal process as well as for a system that undergoes an adiabatic process.
- S3. For an ideal gas , calculate the entropy change of the system that undergoes the above change as well as for more general transformations.
- S4. For selected processes, show by calculation that the entropy change of the universe is always toward increasing the entropy (or keeping it unchanged), never toward decreasing it. (The Second Law of Thermodynamics.)

External Resources (Required):

1. M. Alonso and E. J. Finn, *Physics*, Addison-Wesley, Reading (1970); for access see this module's *Local Guide*.

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ENTROPY

by

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1. Description

The statement that equilibrium for a system of many particles occurs when it is in the state whose partition has the highest probability associated with it, can be translated into a statement about a macroscopic property of this system (a property that can be determined for the bulk system. Pressure, temperature, and volume are similarly macroscopic properties). This statement is the Second Law of Thermodynamics, that systems evolve such that the entropy of the system increases. The concept of entropy and applications of the Second Law are the topic of this module.

2. Suggested Procedure

In AF^1 study sections 13.10 (both of them!), 13.11, and 13.12.

There is a more expanded treatment of this subject in Ford's "Classical and Modern Physics," Vol. 2. Some good illustrations and examples are included. For access, see this module's *Local Guide*.

In AF work problems 13.25, 13.29^{*}, 13.30, 13.31, and 13.33.

3. Comments

You can "derive" AF's Eq. 13.35 without too much difficulty using the First Law of Thermodynamics (Eq. 13.23) in differential form and the ideal gas law (Eq. 13.13). This development is also useful in solving Problems 13.30 and 13.31.

The First Law in differential form is dU = dQ - dW where dW = P dV is the work done by the system (if dV is positive, an increase) For

an ideal gas $U = NE_{k,ave}$ (Eq. 13.4) which is:

U = (3/2)kNT = (3/2)nRT; (n is number of moles)..

So:

$$dQ = (3/2)nR\,dT + P\,dV.$$

The specific heat at constant volume, C_v , is defined as:

$$\frac{dQ}{dt} \equiv C_v,$$

so $C_v = (3/2)nR$. The entropy change is then:

$$dS \equiv \frac{dQ}{T} = \frac{3}{2}nR\frac{dT}{T} + \frac{P}{T}dV.$$

Now for an ideal gas:

$$\frac{P}{T} = \frac{nR}{V},$$

so:

$$dS = \frac{3}{2}nR\frac{dT}{T} + nR\frac{dV}{V}; \quad \text{(ideal gas only)}.$$

Integrating this for a finite transformation we get:

$$S_f - S_i = nR \, \ell n \, \left(\frac{T_f}{T_i}\right)^{3/2} + \, \ell n \, \left(\frac{V_f}{V_i}\right)$$
$$S_f - S_i = nR \, \ell n \, \left(V_f T_f^{3/2}\right) - nR \, \ell n \, \left(V_i T_i^{3/2}\right)$$

So it appears that S at any V and T is:

$$S = nR \, \ell n \, \left(VT^{3/2} \right) + \text{ constant.}$$

[Use the ideal gas law to get this in the form of equation 13.35].

4. Answers to Assigned Problems

13.25 The Carnot cycle on a P-V plot looks like this:

 $^{^1\}mathrm{M.}$ Alonso and E. J. Finn, Physics, Addison-Wesley, Reading (1970). For access, see this module's Local Guide.



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Q = W and you already calculated W above, so that:

$$S_2 - S_1 = \frac{P_1 V_1}{T_1} \, \ell n \, \frac{V_2}{V_1}.$$

The numerical result in AF is correct.

For the constant volume process you should get:

$$S_2 - S_1 = \frac{3}{2} nR \, \ell n \, \frac{T_3}{T_2} = \frac{3}{2} nR \, \ell n \, \frac{P_3 V_3}{P_2 V_2}.$$

Now $V_3 = V_2$ so:

$$S_2 - S_1 = \frac{3}{2} \frac{P_1 V_1}{T_1} \, \ln \frac{P_3}{P_2}$$

Again we get P_3 from $P_3V_3^{\gamma} = P_1V_1^{\gamma}$ and P_2 from $P_2V_2 = P_1V_1$. Then we find:

$$S_3 - S_2 = \frac{3}{2} \frac{P_1 V_1}{T_1} \ln \left(\frac{V_1}{V_2}\right)^{\gamma - 1} = \frac{3}{2} (\gamma - 1) \frac{P_1 V_1}{T_1} \ln \left(\frac{V_2}{V_1}\right)$$

For an ideal gas $\gamma = 5/3$, **not** 1.4, so the factor $(3/2)(\gamma - 1) = 1$ and the entropy change is:

$$S_3 - S_2 = \frac{P_1 V_1}{T_1} \, \ell n \, \frac{V_1}{V_2},$$

which is just the negative of the change $S_2 - S_1$.

13.30

- a. HINT: Use the First Law of Thermodynamics. Note that the container is assumed to be perfectly insulating.
- b. Again an application of dS = (3/2)nR(dT/T) + nR(dV/V), of Eq. 13.35.

13.31 This is not an ideal gas problem, so the above relation cannot be used. Start instead, with the thermodynamic definition of entropy change, dS = dQ/T. The numerical result is correct, using the heat capacity value from Table 13.1. Note the units.

13.33 The numerical answer is correct as given in AF.

Acknowledgments

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13.29 HINT: Refer to the diagram for the Carnot cycle above to tell you the relative slopes of the adiabatic and isothermal processes. For the work done by the gas from stage 1 to stage 2 (the isothermal step) you should get:

$$W = \int_{V_1}^{V_2} P \, dV = nRT \, \ln \frac{V_2}{V_1} = P_1 V_1 \, \ln \frac{V_2}{V_1} = P_2 V_2 \, \ln \frac{V_2}{V_1}.$$

(The numerical answer is correct). For the work done during the adiabatic part of the cycle, from V_3 (= V_2) to V_1 ,

$$W = \int_{V_2}^{V_1} P \, dV = \frac{1}{\gamma - 1} \, \left(P_3 V_2 - P_1 V_1 \right)$$

The P_3 comes from the relation satisfied by adiabatic transformations:

$$P_3 V_3^{\gamma} = P_1 V_1^{\gamma}.$$

The numerical answer given by AF is correct if you use $\gamma = 5/3$, $W = -1.10 \times 10^6$ joules). For the entropy changes involved, use the "ideal gas" expression we derived above for dS. For the isothermal change the first term drops out. (Or equivalently, use the first law of thermodynamics where for an ideal gas dU = 0 for an isothermal process, so dQ = dW,

LOCAL GUIDE

The readings for this unit are on reserve for you in the Physics-Astronomy Library, Room 230 in the Physics-Astronomy Building. Ask for them as "The readings for CBI Unit 160." Do **not** ask for them by book title.

PROBLEM SUPPLEMENT

- 1. Two moles of an ideal gas at $8.31 \times 10^3 \,\mathrm{N/m^2}$ pressure and at temperature -53 °C is placed in contact with a heat reservoir which is maintained at a constant temperature of 127 °C. The gas is allowed to do $6.0 \times 10^3 \,\mathrm{J}$ of work during its contact with the reservoir while its temperature remains constant at -53 °C.
 - a. What is the change in internal energy of the gas? [K]
 - b. How much heat is added to the gas? [F]
 - c. Starting from the thermodynamic definition of entropy find the entropy change of the gas for this process. [H]
 - d. Find the entropy change of the reservoir for this process. [C]
 - e. Find the entropy change of the universe for this process. [J]
 - f. Explain how the Second Law of Thermodynamics applies to the above process. [D]
 - g. Assuming that heat always flows from the reservoir to the gas what is the lowest temperature of the reservoir for which the Second Law is satisfied. Explain. [L]
 - h. The reservoir is removed and the gas is insulated and compressed adiabatically while 5.2×10^3 J of work are done on it. Starting from the thermodynamic definition of entropy, find the entropy change of the gas for this process. [B]
 - i. What is the sign of the entropy change of the universe during this process? [G]
- 2. Suppose we have two large reservoirs of heat, one at $50 \,\mathrm{K}$ and the other at $100 \,\mathrm{K}$. Suppose they are placed in contact. The reservoirs are large enough so that, if $200 \,\mathrm{J}$ of heat are exchanged between them, it doesn't change the temperature of either reservoir.
 - a. Calculate the total entropy change of the universe if 200J of heat flows from the $50 \,\mathrm{K}$ reservoir to the $100 \,\mathrm{K}$ one. [A]
 - b. Calculate the total entropy change of the universe if 200 J of heat flows from the 100 K reservoir to the 50 K one. [M]
 - c. Which of the above processes violates the Second Law and which one satisfies it? [I]

d. Is this consistent with the rule that "heat flows from high temperature to low"? [E]

Brief Answers:

A. $-2 \, J/K$.

B. Zero.

C. $-15 \, \text{J/K}.$

D. See section 13.12 of AF, especially the left-hand column of p. 277.

- G. It increases by virtue of the work done on the gas (whatever does the work experiences an increase in entropy).
- H. +27.3 J/K.
- I. (a) violates 2nd Law, (b) satisfies second law ($\Delta S > 0$).
- J. +12.3 J/K.
- K. Zero.
- L. -53 °C. For any lower temperature the entropy change of gas plus reservoir would be negative, violating 2nd Law.

M. $+2 \, \text{J/K}$.

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E. Yes.

F. 6×10^3 J.