CHAPTER 15

The Laws of Thermodynamics

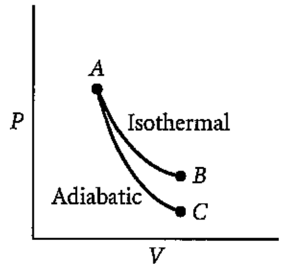
Thermodynamics is the investigation of the energy transferred either as heat (which occurs when thermal equilibrium is sought) or as work (which describes any other transfer of energy). Any object or environment can be considered a **system.** Systems can be **closed**—in which case no mass is transferred to or from outside of the system—or **open.** In this latter case, mass transfer is permissible. A subcategory of the closed system is the **isolated** system, in which there is no energy transferred to or from the system.

The First Law of Thermodynamics

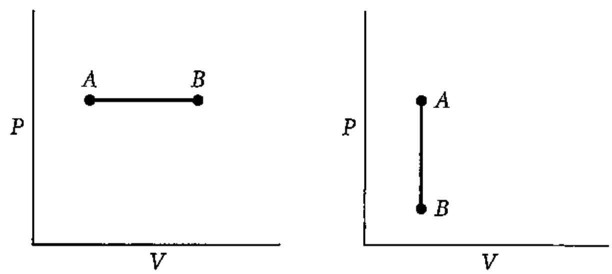
- **The first law of thermodynamics** states that the change in internal energy of a closed system is equal to the difference between heat added and work done. In equation form, $\Delta U = Q - W$. With this equation, heat added to a system and work done by a system are positive quantities, whereas heat lost from a system and work done on a system are negative quantities. This is an expression of **the law of conservation of energy.**
- The AP exam defines W as work done *on* a system. Thus, using this definition the first law of thermodynamics would be expressed as

  $$\Delta U = Q + W$$

  Work done *by* the system would be expressed as a negative quantity.
- By definition, in an isolated system, $W = Q = \Delta U = 0$.
- Work transfer and heat transfer are processes done on or by a system, whereas internal energy is a property of a system.
- In an **isothermal** process, temperature is kept constant. From the ideal gas law, PV is equal to a constant value in a closed system that undergoes an isothermal process. This is idealized in a container with a moveable piston and heat reservoir, which keeps temperature constant as heat is added. Because the internal energy of an ideal monatomic gas is a function of the absolute temperature, if $\Delta T = 0$ then $\Delta U = 0$. Therefore, the work done by the system must be equal to the heat added to the system ($W = Q$). Curves known as **isotherms** can be sketched for changes in pressure and volume on a graph of P vs. V.
- In an **adiabatic** process, heat does not move into or out of the system. As such, internal energy and temperature increase.



- In an **isobaric** process, pressure is constant, so the work done by the system is equal to the product of pressure and the change in volume. When pressure is constant, $W = P\Delta V$.
- In an **isochoric** process, volume is held constant, so the work done on and by the system is zero.



(a) Isobaric (b) Isochoric

Heat Engines

Heat engines turn thermal energy into mechanical work, utilizing a portion of the heat that flows from a high temperature to a low temperature. From the law of conservation of energy, the sum of the work produced and the heat flowing out of an engine must be equal to the heat flowing into an engine.

- The **efficiency** of an engine is defined as the ratio of work produced to the heat flowing in. That is, $e = W/Q_H = 1 - Q_L/Q_H$ since $Q_H = W + Q_L$.
- Real engine processes are irreversible due to the heat unavoidably lost from internal friction. The maximum efficiency for a heat engine, called the **Carnot limit,** is the ratio of temperature change in operation in kelvins to the high temperature of operation: $e_{ideal} = \Delta T/T_H$.
- For refrigerating units, work must be added to cause heat to flow from a lower temperature to a higher temperature. A refrigerator's coefficient of performance is given by the ratio of heat removed to the work inputted. That is, $CP = Q_L/W$. For a Carnot-ideal refrigerator, $CP_{ideal} = T_L/\Delta T$. For heat pumps, the same process applies, but efficiency is measured as the ratio of $CP = Q_H/W$.

The Second Law of Thermodynamics

There are several ways of stating the **second law of thermodynamics.**

- From the **Clausius statement,** heat flows from a warm body to a cool body without outside interference—but not the converse.
- According to the **Kelvin-Planck statement** of the second law of thermodynamics, no engine can turn all heat into work. Absolute Carnot efficiency would require an exhaust temperature of absolute zero, which is impossible.

Entropy and the Second Law of Thermodynamics

The change in **entropy**, or disorder, of a system is the ratio of heat added to a system to the constant temperature in kelvins at which it is added: $\Delta S = Q/T$.

- Within a closed system, the overall entropy always increases, even though there may be isolated localized decreases in entropy.
- As a result of natural processes, entropy will always increase, causing a system to move from a state of order to a state of disorder.
- The categories that keep a system ordered are called **information.** Entropy causes a decrease in a system's information over time.
- Energy loses its capacity to do work over time.

For Additional Review

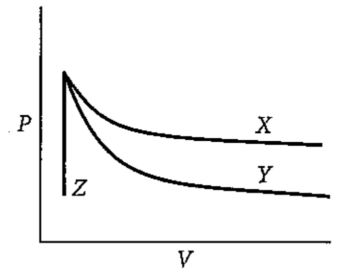
Consider the operational differences (and their resulting implications) for both an ideal engine and a real engine.

Multiple-Choice Questions

1. What is the change in internal energy if 500 J of heat are added to a system, and 125 J of work are done on a system?
   (A) −625 J
   (B) −375 J
   (C) 0 J
   (D) 375 J
   (E) 625 J

Questions 2, 3, and 4 refer to the following *P* vs. *V* graph. The work done is equal to the area under the curve.

2. By which process represented here is the least work done?



   (A) Isobaric
   (B) Isothermal
   (C) Adiabatic
   (D) Isochoric
   (E) None of the above

3. What line or lines represents the process where the most work is done?
   (A) Curve X
   (B) Curve Y
   (C) Curve Z
   (D) Curves X & Z produce the same quantity of work.
   (E) Not enough information is given.

4. Which of the following processes could NOT be represented by this graph?
   (A) Isobaric
   (B) Isothermal
   (C) Adiabatic
   (D) Isochoric
   (E) None of the above

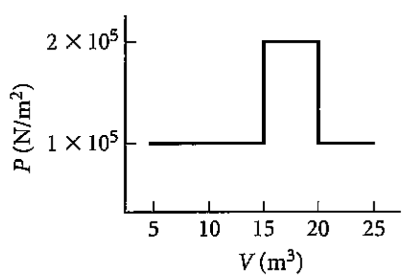
5. In an isobaric process, what is the net work by an ideal gas of pressure, *P*, which expands to three times its original volume *V*?
   (A) $3P/V$
   (B) $2PV$
   (C) $P/3V$
   (D) $PV/3$
   (E) PV^3

6. What is the limit of efficiency for an engine that runs between 100°C and 150°C?
   (A) 7%
   (B) 12%
   (C) 17%
   (D) 25%
   (E) 31%

7. What is the ratio of actual efficiency to optimal efficiency for an engine whose rate of heat input is 250 J/s at 227°C and whose rate of heat output is 225 J/s at 152°C?
(A) 3/2
(B) 2/1
(C) 1/1
(D) 1/2
(E) 2/3

8. If the heat of vaporization of water is 539 kcal/kg, what is the change in entropy of 1 kg of water as it turns entirely to steam at 100 degrees?
(A) 0.14 cal/K
(B) 1.4 cal/K
(C) 14 cal/K
(D) 140 cal/K
(E) 1400 cal/K

Question 9 refers to the diagram below.



9. In this process, what is the work done as volume changes from 5 m^3 to 25 m^3?
(A) 5×10^5 J
(B) 10×10^5 J
(C) 15×10^5 J
(D) 20×10^5 J
(E) 25×10^5 J

10. Which of the following is NOT a statement of the second law of thermodynamics?
I. Net entropy increases in the universe over time.
II. 100% efficiency is impossible.
III. Internal energy is equal to heat added less the work done by a system
(A) I only
(B) II only
(C) III only
(D) I and II
(E) II and III

Free-Response Questions

1. (a) In theory, at what temperature should heat output be such that the actual efficiency of an engine is equal to optimal efficiency for an engine whose rate of heat input is 1330 J/s at 375°C and whose heat output is 800 J/s?
(b) Each second, how much work is done in this process?

2. Sketch a P vs. V graph of an isobaric process such that the work done is 2.5×10^5 J at initial pressure of 2×10^5 Pa, and initial volume of 0.7 m^3.

ANSWERS AND EXPLANATIONS

Multiple-Choice Questions

1. (E) is correct. From the first law of thermodynamics, $\Delta U = Q - W$. Recalling the sign conventions, in which heat added is a positive value and work done on a system is a negative value,
$\Delta U = Q - W = +500 \text{ J} - (-125 \text{ J}) = 625 \text{ J}$.
For Questions 2, 3, 4: Curve X represents an isothermal process, curve Y represents an adiabatic process, and curve Z represents an isochoric process.

- **2. (D) is correct.** The work done is equal to the area under the curve of each process. Since the vertical line Z represents this process, the area under the isochoric curve is zero.
- **3. (A) is correct.** The work done is equal to the area under the curve of each process. The area under curve X has the greatest area.
- **4. (A) is correct.** Of the processes mentioned, a horizontal line representing constant pressure is not pictured. This is called an isobaric process.
- **5. (B) is correct.** In the work done by an isobaric process, the change in pressure is the product of pressure and the change in volume. As such, $W = P(3V - V) = 2PV$.
- **6. (B) is correct.** The limit of efficiency, the Carnot efficiency, of a heat engine is given by the quotient of the change in temperature to the high temperature of heat input in kelvins, which is 50 K/423 K = 0.12, 12% efficiency.
- **7. (E) is correct.** The actual efficiency of a heat engine—given by the quotient of the change in heat input and output to the heat input—is 25 J/s/250 J/s = 0.10 = 10% efficiency. The Carnot efficiency is given by the quotient of the change in temperature to the high temperature of heat input in kelvins, which is 75 K/500 K = 0.15 = 15% efficiency. The ratio 10% to 15% is 2:3.
- **8. (E) is correct.** Since the heat of vaporization of water is 539 kcal/kg, the heat required to turn water to steam is (1 kg)(539 kcal/kg) = 539 kcal. The change in entropy is 539 kcal/373 K = 1.4 kcal/K, which is 1400 cal/K.
- **9. (E) is correct.** Since work done is the area under the curve, the work done will be the sum of the following. As the volume changes from 5 m^3 to 15 m^3, the work done is $(10\ m^3)(1 \times 10^5\ N/m^2) = 10 \times 10^5$ J; the work done as the volume changes from 15 m^3 to 20 m^3 is $(5\ m^3)(2 \times 10^5\ N/m^2) = 10 \times 10^5$ J; and the work done as the volume changes from 20 m^3 to 25 m^3 is $(5\ m^3)(1 \times 10^5\ N/m^2) = 5 \times 10^5$ J. The total work done is therefore 25×10^5 J.
- **10. (C) is correct.** Items I and II are statements of the second law of thermodynamics, whereas item III is a statement of the first law of thermodynamics.

Free Response Questions

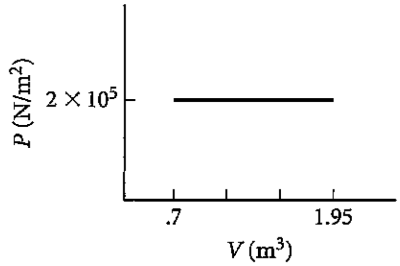
1. (a) The actual efficiency of a heat engine is given by the quotient of the change in heat input and output to the heat input, 530 J/s/1330 J/s = 40% efficiency. The Carnot efficiency is given by the quotient of the change in temperature to the high temperature of heat input in kelvins. Therefore $0.40 = (648\ K - T_L)/648$ K. Solving for the low temperature at the output, $T_L = 389\ K = 116°C$.

   (b) The values for heat input and output are given in joules per second, $\Delta Q = 1330\ J - 800\ J = 530$ J.

   This response uses the definitions of Carnot efficiency and real engine efficiency to find the unknown temperature. Celsius is converted to kelvins as required.

2. In an isobaric process, pressure is constant, so initial pressure will be the same as final pressure. A horizontal line will graphically represent this. If the work done is 2.5×10^5 J, the change in volume should be the quotient of work done

to pressure. $W/P = \Delta V = 2.5 \times 10^5\ \text{J}/2 \times 10^5\ \text{N/m}^2 = 1.25\ \text{m}^3$. If the initial volume is $0.7\ \text{m}^3$, the final volume should be $1.95\ \text{m}^3$. The sketch should look something like the one shown below.



This response gives a well-reasoned explanation of how the system described should be graphically depicted, as well as presenting a graph. The vertical axis is quantified after a value for pressure is found.