

Thermodynamics

The study of temperature, heat and related macroscopic properties (length, volume, pressure, and electrical resistance) comprises the branch of physics called thermodynamics.

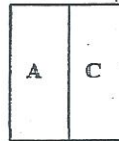
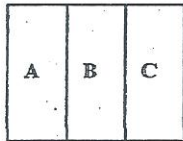
Thermodynamic equilibrium

When two systems are placed together (in thermal contact) until no further change occurs in any macroscopic property, then the two have reached thermodynamic equilibrium with each other.

* Two systems have the same temperature if they are in thermodynamic equilibrium.

Zero law of thermodynamics:

If two systems A and C each are in thermodynamic equilibrium with system B, then A and C are in thermodynamic equilibrium with each other.



Temperature scales

The temperature scales in common use are Celsius ($^{\circ}\text{C}$), Kelvin (K), Fahrenheit ($^{\circ}\text{F}$), and Rankine ($^{\circ}\text{R}$). The latter two are largely limited to the United States. One Celsius degree represents the same temperature difference as one Kelvin, but the zero of the Celsius scale occurs at 273.15 K, so

$$T_{\text{C}} = T - 273.15,$$

where:

T_{C} = temperature on the Celsius scale

T = temperature on the Kelvin scale.

* The relation between the Fahrenheit and Celsius is

$$T_{\text{F}} = (9/5) T_{\text{C}} + 32$$

Temperature and heat

Heat is energy being transferred from one object to another because of a temperature difference alone.

* Strictly speaking, the word heat refers only to energy in transit. Once heat has been transferred to an object, we say that the internal energy of the object has increased, but not that it contain more heat.

Heat capacity and specific heat

Experimentally, we find the heat ΔQ transferred to an object and the resulting change ΔT in the object's temperature is directly proportional. We write

$$\Delta Q = C \Delta T,$$

where C is called the heat capacity of the object, and its unit is J/K. The heat capacity applies to a specific object depends on its mass and on the substance from which it's made. We characterize different substances in terms of specific heat c , or heat capacity per unit mass. The heat capacity of an object is then the product of its mass and specific heat, so we can write

$$\Delta Q = cm \Delta T,$$

* The calorie (cal) was defined as the heat needed to raise the temperature of one gram of water from 14.5°C to 15.5°C, (cal = 4.184 J).

* The British thermal unit (BTU) was defined as the heat needed to raise the temperature of one pound of water from 63°F to 64°F, and is equal to 1055 J.

The equilibrium temperature

If two objects are thermally insulated from their surroundings, then all the energy leaving the hotter object ends up in the cooler one. Mathematically, this statement may be written

$$m_1 c_1 \Delta T_1 + m_2 c_2 \Delta T_2 = 0$$

where mc is the heat capacity of an object of mass m and specific heat c , and ΔT is the temperature change of that object. For the hotter object, ΔT is negative.

Heat transfer

Three heat-transfer mechanisms commonly occur. These are:

- Conduction;** a process involving direct physical contact,
- Convection;** involving energy transfer by the bulk flow of fluid,
- Radiation;** energy transferred by electromagnetic waves.

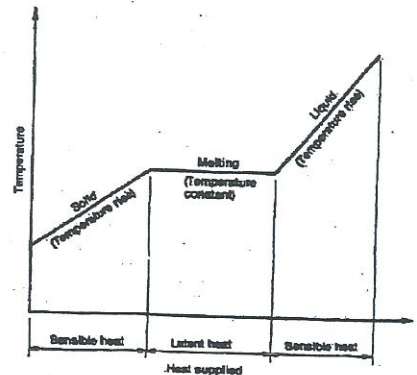
Thermal Behavior of Matter

Phase changes, Thermal expansion, Thermal stress.

The ideal gas law

$$PV = NkT,$$

With P , V and T the pressure, volume, and temperature, respectively, and N the number of molecules in the gas, The constant k is Boltzmann's constant, it's value is



$$k = 1.38 \times 10^{-23} \text{ J/K}$$

One mole of anything consists of Avogadro's number of that thing, where Avogadro's number is approximately $N_A = 6.022 \times 10^{23}$.

If we have n moles of gas, then $N = nN_A$ $kT = nRT$, where the constant $R = N_A k = 8.314 \text{ J/K.mol}$ is called the universal gas constant.

Heat, Work, and the first law of thermodynamics

The first law of thermodynamics:

The change in the internal energy of a system depends only on the net heat transferred to the system and the net work done by the system, and its independent of the particular processes involved.

Mathematically; the law reads

$$\Delta U = Q - W,$$

where ΔU is the change in a system's internal energy, Q the heat transferred to the system, and W the work done by the system.

Thermodynamic processes

Work and volume change

Since $\Delta W = F \Delta x$,
then $\Delta W = PA \Delta x = P \Delta V$.

To find the work associated with a large volume change, we take the limit $\Delta V \rightarrow 0$, and integrate over the volume change:

$$W = \int dW = \int_{V_1}^{V_2} P dV,$$

where V_1 and V_2 are the initial and final volumes. The figure shows the geometrical interpretation of this equation: the work done by the gas is simply the area under the PV curve.

Isothermal Processes

The system moves from its initial state to its final state along a curve of constant temperature- an **isotherm**.

For the ideal gas, we can relate pressure P and volume V through the ideal gas law

$$P = \frac{nRT}{V}$$

The work equation becomes

$$W = \int_{V_1}^{V_2} \frac{nRT}{V} dV$$

For an isothermal process, the temperature T is constant, giving

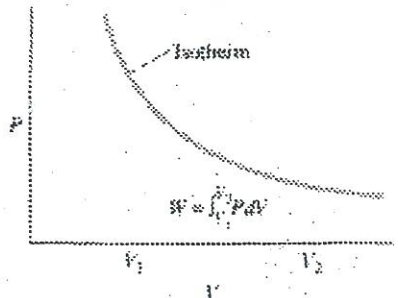
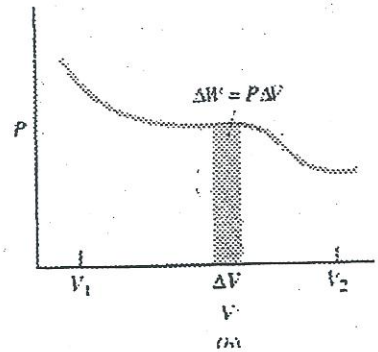
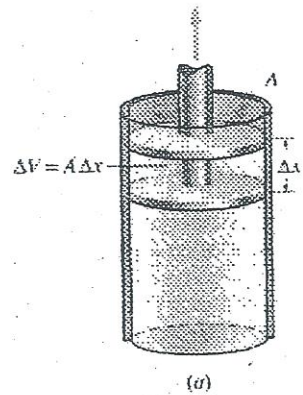


FIGURE PV diagram for an isothermal process, showing a particular isotherm—a curve of constant temperature. Since $PV = nRT$ for an ideal gas, the pressure and volume are inversely related at constant temperature, so the isotherm is a hyperbola. The work done during an isothermal expansion from volume V_1 to V_2 is the area under the isotherm.

$$W = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln V \Big|_{V_1}^{V_2} = nRT \ln \left(\frac{V_2}{V_1} \right)$$

Since there is no change in the temperature during an isothermal process, then there will be no change in the internal energy of the ideal gas. The first law of thermodynamics then gives

$$\Delta U = 0 = Q - W$$

So

$$Q = W = nRT \ln \left(\frac{V_2}{V_1} \right) \quad (\text{isothermal process})$$

Constant-volume processes and the specific heat

In this process the gas does no work, and the first law of thermodynamics becomes simply

$$Q = \Delta U$$

To express this result in terms of a temperature change ΔT , we introduce the molar specific heat at constant volume, C_v , defined by the equation

$$Q = nC_v \Delta T \quad (\text{constant-volume processes})$$

where n is the number of moles. This molar specific heat, with the gas it's more convenient to consider the heat per mole rather than per unit mass. Introducing the definition of C_v into the first equation gives

$$nC_v \Delta T = \Delta U$$

Solving for C_v then

$$C_v = \frac{1}{n} \frac{\Delta U}{\Delta T}$$

Isobaric processes and specific heat

In a reversible isobaric process, a system moves along an isobar, or curve of constant pressure, in its PV diagram. The work done as the volume changes from V_1 to V_2 is the area under the isobar, or

$$W = P (V_2 - V_1) = P \Delta V$$

Solving the first law for Q and using our expression for work gives

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

For an ideal gas, we have just found that the change in internal energy is given by

$$Q = nC_v \Delta T + P \Delta V$$

For an ideal gas undergoing an isobaric process. We define the **molar specific heat at constant pressure**, C_p , as the heat required to raise one mole of gas through a unit temperature change at constant pressure, or

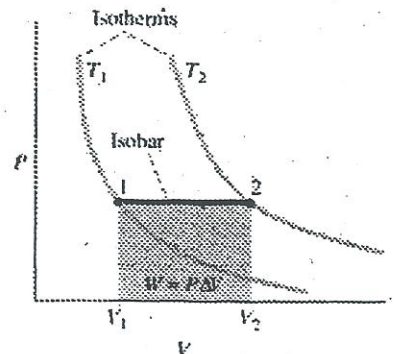


FIGURE P-V diagram for an isobaric process. The gas moves along the isobar from state 1 to state 2, doing work $P\Delta V$ in the process. Also shown are isotherms for the initial and final temperatures.

$$Q = nC_P \Delta T$$

The equation (*) can be written

$$nC_P \Delta T = nC_V \Delta T + P \Delta V \text{ (isobaric process)}$$

The ideal gas law, $PV = nRT$, allows us to write

$$P \Delta V = nR \Delta T,$$

for the isobaric process. Using this expression in Equation (*) gives

$$nC_P \Delta T = nC_V \Delta T + nR \Delta T,$$

so

$$C_P = C_V + R.$$

Adiabatic processes

In an adiabatic processes, no heat transfer occurs between a system and its environment. Since the heat Q is zero in an adiabatic process, the first law becomes simply

$$\Delta U = -W. \text{ (adiabatic process)}$$

The shape of the adiabatic path is

$$P V^\gamma = \text{constant} = P_0 V_0^\gamma$$

where $\gamma = C_P/C_V$ is the ratio of the specific heats and P_0 and V_0 are the values of P and V at some reference point, which could be any point in the process.

Because $C_P = C_V + R$, the ration $\gamma = C_P/C_V$ is always greater than 1.

We can find the temperature change in an adiabatic process by using the ideal gas law to eliminate pressure form the above equation. Writing that equation in the form

$$PV V^{\gamma-1} = P_0 V_0 V_0^{\gamma-1}$$

and substitute for PV from the ideal gas law gives

$$nRT V^{\gamma-1} = nRT_0 V_0^{\gamma-1}$$

Dividing both side by nR gives

$$T V^{\gamma-1} = T_0 V_0^{\gamma-1}$$

How much work is done during an adiabatic process?

Since there's no heat transfer, $W = -\Delta U$. But we've found that $\Delta U = nC_V \Delta T$ for any process.

Therefore in an adiabatic process

$$W = -nC_V \Delta T = -\frac{nC_V R (T_1 - T_2)}{R}$$

$$= -\frac{C_V (P_1 V_1 - P_2 V_2)}{R}$$

$$PV = nRT$$

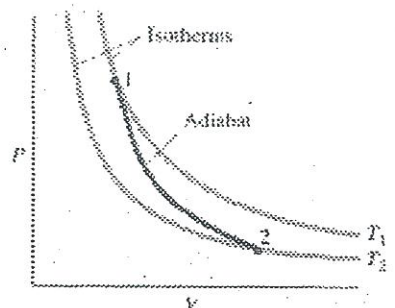


FIGURE: P-V curve for an adiabatic process (red) shows that the pressure drops more than in an isothermal process going between the same two volumes. Two isotherms shown are for the initial and final temperatures of the adiabatic process. The adiabatic path is steeper because the gas loses internal energy as it does work.

where T_1 and T_2 are the initial and final temperatures. We can express this result in terms of pressure and volume change by solving the ideal gas law, $PV = nRT$, for temperature and using the result in the equation above:

$$W = nC_V \frac{P_1V_1 - P_2V_2}{R} = \frac{C_V}{R} (P_1V_1 - P_2V_2)$$

But $R = C_P - C_V$, so

$$\frac{C_V}{R} = \frac{C_V}{C_P - C_V} = \frac{1}{(C_P/C_V) - 1} = \frac{1}{\gamma - 1}$$

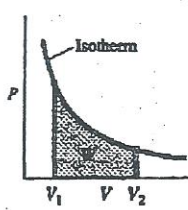
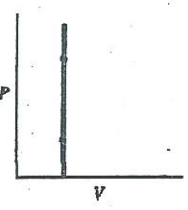
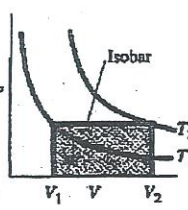
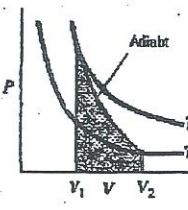
Then our expression for the adiabatic work becomes

$$W = \frac{P_1V_1 - P_2V_2}{\gamma - 1}$$

Cyclic Processes

Many natural and technological systems undergo cyclic processes, in which the system returns periodically to the same thermodynamic state. Cyclic processes often involve the four simple processes we've just outlined which are summarized in the Table below. We've seen that the work done in any reversible process is just the area under the PV curve describing that process. A cyclic process returns to the same point in the PV diagram, so it generally involves both expansion and compression of the gas (Fig. *). During expansion of the gas does work on its surroundings; during compression work gets done on the gas. The net work is the difference between the two. Figure *-b shows that this work is the area measured as pressure times volume enclosed by the cyclic path in the PV diagram.

TABLE Ideal Gas Processes

	ISOTHERMAL	CONSTANT-VOLUME	ISOBARIC	ADIABATIC
PV diagram				
Defining characteristic	$T = \text{constant}$	$V = \text{constant}$	$P = \text{constant}$	$Q = 0$
First law	$Q = W$	$Q = \Delta U$	$Q = \Delta U + W$	$\Delta U = -W$
Work done by gas	$W = nRT \ln\left(\frac{V_2}{V_1}\right)$	0	$W = P(V_2 - V_1)$	$W = \frac{P_1V_1 - P_2V_2}{\gamma - 1}$
Other relations	$PV = \text{constant}$	$Q = nC_V\Delta T$	$Q = nC_P\Delta T$ $C_P = C_V + R$	$PV^\gamma = \text{constant}$ $TV^{\gamma-1} = \text{constant}$

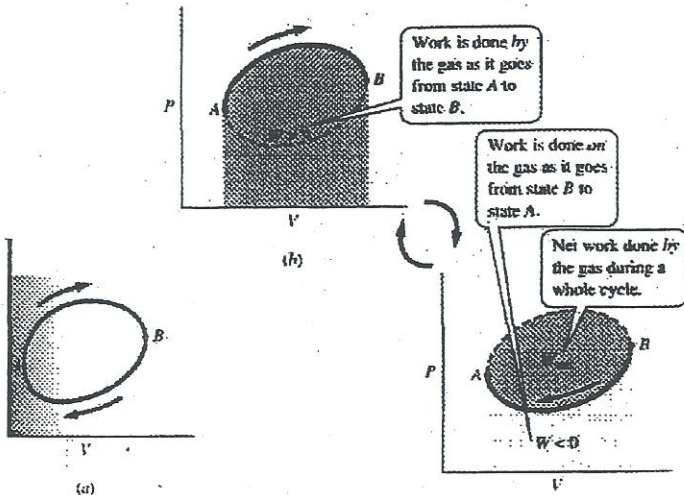
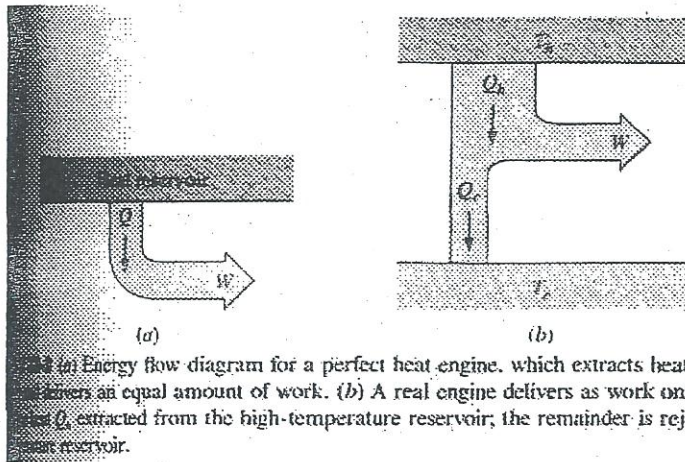


FIGURE (a) A cyclic path for an ideal gas, traversed clockwise in the PV diagram. (b) The work done during a cycle. Work is done by the gas as it goes from state A to state B, and work is done on the gas as it returns from state B to state A. Since the area under each curve represents the associated work, the area inside the cycle represents the net work done by the gas. If the cycle were traversed counterclockwise rather than clockwise, the area inside the cycle would instead be the net work done on the gas.

The second law of thermodynamics

It is impossible to construct a heat engine operating in a cycle that extracts heat from a reservoir and delivers an equal amount of work.



It is impossible to convert all the internal energy of a system to useful work. But devices called heat engines can extract some of that internal energy. Examples of heat engine include gasoline and diesel engines.

A simple heat engine consists of a gas-cylinder system and a heat reservoir, the later kept hot, perhaps, by burning a fuel. With the gas initially at high pressure, we place the cylinder in contact with the heat reservoir. The gas expands and does work W on the piston. In this isothermal process, the gas extracts heat $Q = W$ from the reservoir. Eventually the gas reaches pressure equilibrium and stops expanding. The piston must then be returned to its original position if it's to do more work.

If we just push the piston back, we'll have to do as much work as was extracted during the expansion, and or engine will produce no net work. Instead we can cool the gas to reduce its volume, through thermal contact with a cool reservoir. But then some energy leaves the system as heat rather than work, as shown conceptually in the figure. Our engine extracts heat from a source and delivers mechanical work, but over a full cycle the amount of work is always less than the heat extracted. The remaining energy is rejected to the lower temperature reservoir, usually environment. In practical terms, much of the energy released from fuels in car and power plants ends up as waste heat.

We define the **efficiency** of an engine as the ratio of work W output by the engine in one cycle on the heat Q_h absorbed from the high-temperature reservoir.

$$e = \frac{W}{Q_h}$$

Since the process is cyclic, there's no net change in internal energy over one cycle. Then the first law of thermodynamics, $\Delta U = Q - W$, ensures that the work done is the difference between the heat Q_h extracted from the high-temperature reservoir and the heat Q_c rejected to the cool reservoir. So the efficiency is

$$e = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$$

The figure shows a simple heat engine whose efficiency we can readily calculate. The engine consists of a cylinder containing an ideal gas, sealed by movable piston. The piston is connected to a rod that drives a wheel, as the piston goes back and forth, the wheel turns continually. The engine gets its energy from a heat reservoir maintained at a high temperature T_h , and it rejects heat to a cooler reservoir at temperature T_c . The figure shows how the engine works. It starts with the piston in its leftmost position, so the gas volume is at its minimum. This state is point A in the PV diagram of the figure. At this point, we bring the high-temperature reservoir into thermal contact with the cylinder. The gas absorbs an amount of heat Q_h from the hot reservoir and expands isothermally along path AB in the PV diagram. Since the temperature remains constant during this process, so does the internal energy. The first law then shows that the engine does work $W = Q$ on the piston and wheel. At state B, we remove the hot reservoir. The expansion is now adiabatic, and follows path BC in the PV diagram. We design the engine so that, when the piston reaches its rightmost position, the gas temperature has cooled to T_c . This state is point C in the PV diagram, and is the state of maximum gas volume. We bring the cool reservoir into thermal contact with the cylinder. The wheel's inertia keeps it turning, and the wheel does work on the gas, compressing it isothermally from state C to state D. This work ends up as heat rejected to the cool reservoir. Finally at state D, we remove the cool reservoir from the contact with the cylinder and allow the compression to continue adiabatically until the gas temperature has risen to T_h and the piston is once again in its leftmost position, with the gas compressed to its minimum volume.

The engine we have just described undergoes a cyclic process consisting of four reversible steps, two isothermal and two adiabatic. This cycle is called a Carnot cycle, and the engine Carnot engine.

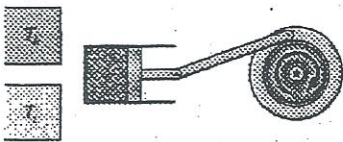
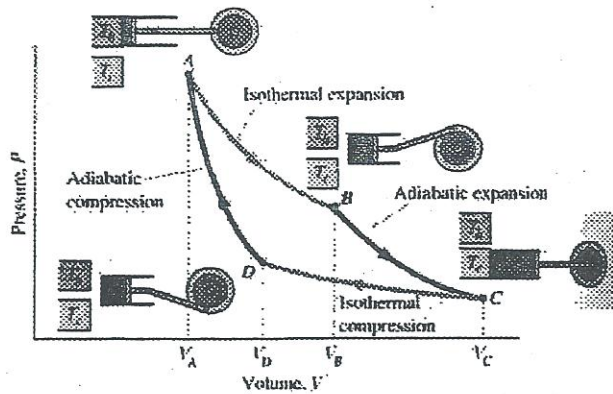


FIGURE A simple heat engine. The gas absorbs heat from the hot reservoir, does work on the piston and wheel, and rejects heat to the cool reservoir. The two heat reservoirs can be moved to bring either one into thermal contact with the cylinder.

FIGURE PV diagram for the engine of Fig. 22-5. AB and DC are isotherms at the temperatures of the hot and cool reservoirs, respectively; AD and BC are adiabatic curves.



To find out what is the efficiency of Carnot engine, we need the heats Q_h and Q_c absorbed and rejected during the isothermal parts of the cycle shown in the figure. We develop Equation (*) to deal with such isothermal processes. Applying the equation gives the heat Q_h absorbed during the isothermal expansion AB:

$$Q_h = nrT_h \ln\left(\frac{V_B}{V_A}\right), \quad \text{--- (*)}$$

and the heat Q_c rejected during the isothermal compression CD:

$$Q_c = -nrT_c \ln\left(\frac{V_D}{V_C}\right) = nrT_c \ln\left(\frac{V_C}{V_D}\right). \quad \dots \quad (**)$$

We put the minus sign here because our statement of the first law describes Q as the heat absorbed, while equation (**) for the engine efficiency requires that Q_c be the heat rejected. To calculate engine efficiency according to the equation (**), we need the ratio Q_c/Q_h :

$$\frac{Q_c}{Q_h} = \frac{T_c \ln(V_C/V_D)}{T_h \ln(V_B/V_A)}$$

This expression can be simplified by applying equation (*) to the adiabatic processes BC and DA in the Carnot cycle:

$$T_h V_B^{\gamma-1} = T_c V_C^{\gamma-1} \quad \text{and} \quad T_h V_A^{\gamma-1} = T_c V_D^{\gamma-1}$$

Dividing these two equations gives

$$\frac{T_c}{T_h} = \left(\frac{V_B}{V_A}\right)^{\gamma-1} = \left(\frac{V_C}{V_D}\right)^{\gamma-1} \quad \text{or} \quad \left(\frac{V_B}{V_A}\right) = \left(\frac{V_C}{V_D}\right)$$

So the equation becomes simply

$$\frac{Q_c}{Q_h} = \frac{T_c}{T_h}$$

Using this result, then the Carnot engine efficiency is:

$$e_{\text{Carnot}} = 1 - \frac{T_c}{T_h}$$

Where the temperatures are measured on an absolute scale (Kelvin), the above equation tells us that the efficiency of a Carnot engine depends only on the highest and lowest temperatures of the working fluid. For a practical engine, the low temperature is usually the ambient temperature of the environment. Then to maximize the efficiency, we must make the high temperature as high as possible. Real engines represent a compromise between efficiency and the ability of materials to withstand high temperatures and pressures.

Example (A Carnot Engine)

A Carnot engine extracts 240 J of heat from a high-temperature reservoir during each cycle. It rejects 100 J of heat to a reservoir at 15°C. How much work does the engine do in one cycle? What is its efficiency? What is the temperature of the hot reservoir?

Solution

The first law of thermodynamics requires that energy not rejected as heat be delivered as work, so the engine does

$$W = 240 \text{ J} - 100 \text{ J} = 140 \text{ J}$$

of work. The efficiency is defined by equation (*) as the ratio of work to heat extracted from the hot reservoir:

$$e = \frac{W}{Q_h} = \frac{140\text{ J}}{240\text{ J}} = 0.583 = 58.3 \text{ percent}$$

Knowing the efficiency, we can solve equation (*) for the high temperature to get

$$T_h = \frac{T_c}{1-e} = \frac{288\text{ K}}{1-0.583} = 691\text{ K} = 418^\circ\text{ C}$$

Exercise:

A Carnot engine operates between heat reservoirs at 520 K and 280 K. (a) What is its efficiency? (b) If it produces useful work at the rate of 400 W, at what rate does it reject waste heat? ((a) 46%, (b) 467 J)

* Physics (With Modern Physics For Scientists and Engineers.
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