

The Big Ideas—Chapter 22

(Serway and Beichner, Physics for Scientists and Engineers, 5th Edition)

<p><i>Section 1</i></p> <p>A cyclic process may be exploited to construct a “heat engine”—a device that trades heat from a hot reservoir for work at the cost of some exhaust or waste heat—or a “heat pump” (or “refrigerator”)—a device that causes heat to flow from cold reservoirs to hot reservoirs with the necessary expenditure of mechanical energy.</p> <p>In both cases we distinguish between the heat <i>to</i> the system <i>from</i> the “hot” reservoir—Q_h—and the heat <i>from</i> the system <i>to</i> the “cold” reservoir—Q_c. The first law of thermodynamics connects these heats with the net work done per cycle.</p> <p>A “perfect heat engine” is one for which there is no waste heat, that is, it uses all heat <i>from</i> the hot reservoir to do <i>work</i>. A “perfect heat pump” is one that requires no work input, that is, it simply causes heat to flow from the cold reservoir to the hot reservoir.</p> <p>Although both perfect heat engines and perfect refrigerators are <i>completely</i> compatible with the first law of thermodynamics, they are not allowed by nature. These observations form the basis for the Kelvin-Planck and Clausius statements of the “Second Law of Thermodynamics.”</p> <p>We define the efficiency of a heat engine as the ratio of the work done per cycle to the heat from the hot reservoir per cycle usually expressed as a percentage. The second law of thermodynamics says that the efficiency is always less than 100%.</p>	$W = Q_h - Q_c$ <p>Perfect heat engine: $Q_c = 0$</p> <p>Perfect heat pump: $W = 0$</p> <p><u>2nd Law of Thermo</u></p> <p>Kelvin-Planck: No such thing as a perfect heat engine.</p> <p>Clausius: No such thing as a perfect heat pump.</p> $e = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$
<p><i>Section 2</i></p> <p>A reversible process is one for which all changes in the system and its surroundings can be “undone” restoring both precisely to their initial states. Any process that involves friction, viscosity, or any other mechanism for “dissipating” energy is irreversible. Almost all real processes <i>do</i> involve some level of dissipation and are, therefore, irreversible.</p> <p>Dissipation does <i>not</i> involve the “destruction” of energy, only its conversion from accessible forms like gravitational potential</p>	

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<p>energy, bulk kinetic energy, and very hot, concentrated gases into less accessible internal forms like very large bodies of cool dilute fluids.</p> <p>Some examples: Dropping an egg onto the floor. Diving into a swimming pool. A bouncing ball bouncing lower and lower. A mug of hot coffee floating in the cold ocean.</p> <p>In a reversible process, both the system and its surroundings are <i>at all times</i> in a well-defined thermodynamic equilibrium state. For instance, if the system were a gas, we would know precisely what it's temperature, volume, and pressure were at all times and be able to draw the "path" of the process on a <i>PV</i> diagram.</p> <p>Processes that occur spontaneously always involve systems that are not in well defined thermodynamic equilibrium states and are, therefore, irreversible.</p>	
<p><i>Section 3</i></p> <p>Heat engines and heat pumps based on the Carnot cycle have the maximum possible theoretical efficiency for any engine operating between any given temperature extremes.</p> <p>This is because the Carnot cycle involves heat <i>input</i> that comes entirely <i>from</i> a single reservoir at the highest temperature encountered and heat <i>output</i> that goes entirely <i>to</i> a single reservoir at the lowest temperature encountered.</p> <p>In the Carnot cycle <i>all</i> heat <i>input</i> occurs during a high temperature isothermal expansion and <i>all</i> heat <i>output</i> occurs during a low temperature isothermal compression. An adiabatic expansion links the high temperature expansion to the low temperature compression and an adiabatic compression links the low temperature compression back to the high temperature expansion.</p>	$e_{\max} = e_{\text{Carnot}} = 1 - \frac{T_c}{T_h}$ $\frac{T_c}{T_h} = \frac{Q_c}{Q_h}$
<p><i>Section 4</i></p> <p>Gasoline and diesel engines make use of less than ideal, but practical cyclic processes.</p> <p>These processes provide good examples of calculating thermodynamic efficiencies.</p>	

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<p><i>Section 5</i></p> <p>Heat pumps and refrigerators are rated in terms of coefficients of performance which are never greater than those of devices based on a Carnot cycle operating between the same two extreme temperatures.</p> <p>In both cases we care about a ratio of heat to work. For a heat pump we want maximum heat output (to the high temperature “reservoir”) for minimum work. For a refrigerator we want maximum heat input (from the low temperature “reservoir”) for minimum work.</p>	<p>Heat pump:</p> $COP^{hp} = \frac{Q_h}{W}$ $COP_{\max}^{hp} = COP_{\text{Carnot}}^{hp} = \frac{1}{1 - T_c / T_h}$ <p>Refrigerator:</p> $COP^r = \frac{Q_c}{W}$ $COP_{\max}^r = COP_{\text{Carnot}}^r = \frac{1}{T_h / T_c - 1}$
<p><i>Section 6</i></p> <p>The Second Law of Thermodynamics reveals the existence of a previously unknown “state variable” (like volume, pressure, temperature, and energy) called “entropy.” Like all state variables, the change in the entropy of a system <i>does not depend</i> on the process. In any infinitesimal process, the associated infinitesimal change in entropy of a system is equal to the infinitesimal heat transfer to the system divided by the absolute temperature.</p> <p>Since the change in entropy of a system is <i>not</i> path dependent, it can always be calculated—even for processes that are highly irreversible—by devising an imaginary quasistatic process that accomplishes the <i>same</i> overall change and calculating the entropy change for <i>that</i> process.</p> <p>For an ideal gas we find a particularly simple equation linking the change in entropy of an ideal gas to its heat capacity and other state variables.</p>	$dS = \frac{dQ}{T}$ $S = \int_{\text{reversible path}} \frac{dQ}{T}$ $S_{\text{ideal gas}} = n C_V \ln \frac{T_f}{T_i} + R \ln \frac{V_f}{V_i}$

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<p><i>Section 7</i></p> <p>The entropy of an isolated system <i>cannot</i> decrease. If an irreversible process takes place, the entropy <i>increases</i>.</p> <p>This is a beautifully succinct and mathematically rigorous expression of the Second Law of Thermodynamics. It is the <i>only</i> fundamental law of physics that provides a basis for distinguishing between the “future” and the “past.” That is, if the entropy of an isolated system is <i>different</i> at two different <i>times</i>, then the time associated with the <i>smaller</i> entropy was necessarily <i>earlier</i> than that associated with the <i>larger</i> entropy!</p> <p>This statement of the Second Law provides new meaning to the phrase “irreversible process”: Every irreversible process <i>unalterably</i> increases the entropy of the universe!</p>	$\left. \frac{dS}{dt} \right _{\text{isolated system}} = 0$
<p><i>Section 8</i></p> <p>The entropy of a system is associated at the microscopic level with the number of ways one can distribute the constituents of a system and the energy of the system among those constituents. The larger the number, the greater the entropy.</p> <p>The entropy of a system generally increases when it gets more volume to occupy or more energy to distribute among its constituents.</p>	$S = k_B \ln W$