

Thermodynamics Review

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Alternative Energy

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Reading for today: Chapter 5

Reading for Monday: Combustion notes

Reading for next Wednesday: Engineering economics notes

Homework assignment due next Monday, February 1.

Combustion notes posted on-line give details of derivations for equations to be presented in Wednesday lecture. If you are comfortable with using the equations that are presented in that lecture you do not have to study these notes.

Today's Class

- Review last class
- Thermodynamic properties
- First law: energy balance
- Second law: entropy and the most efficient process
- Thermodynamic cycles
 - Engine cycles
 - Refrigeration cycles

Thermodynamics is the basic science of energy and energy transformations. Any analysis of energy processes is rooted in the first law of thermodynamics which gives a balance between heat transfer, work, and internal energy of substances.

The second law of thermodynamics tells us that there is a maximum efficiency for the conversion of heat to work. This uses the thermodynamic property entropy to calculate this maximum efficiency.

Practical energy transfer processes use the chemical energy in fuels to produce heat. The analysis of chemical energies, particularly the energy in fuels, will be considered in the next class.

A key element in energy transfer processes is the notion of a cycle. Engine cycles transform heat into work; refrigeration cycles are used to transfer heat from a low temperature to a higher temperature. Figures of merit for these cycles

Resources vs. Reserves

	Known	Unknown
Economical to Recover	Reserves	Resources
Not economical to recover	Resources	Resources

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Note that resources can move into reserves in two ways: by exploratory surveys that give a good measure of the material in place (moving from unknown to known) and by new technology (or increases in price) that make a material newly economic to recover. For oil, the ability to drill offshore and to drill deeper wells has allowed more oil-in-place to be economically produced.

The reserves in an existing oil field have been observed to grow as the field produces oil. This is due to the increased knowledge about the oil present and the ability to better predict how much oil can be developed.

Reference: http://www.spe.org/spe/jsp/basic/0,2396,1104_12171_0,00.html#fig1

Organizations are the Society of Petroleum Engineers, the World Petroleum Council, and the American Association of Petroleum Geologists.

CONTINGENT RESOURCES. estimated to be potentially recoverable from known accumulations, but which are not currently considered to be commercially recoverable.

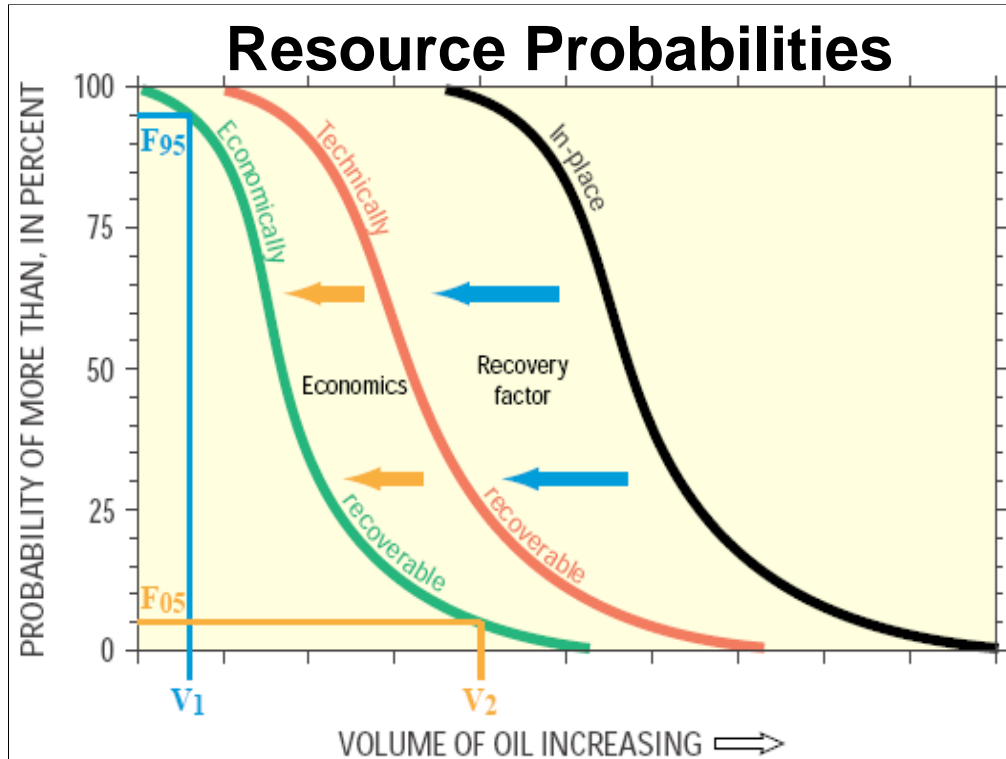
UNDISCOVERED PETROLEUM-INITIALLY-IN-PLACE. petroleum which is estimated to be contained in accumulations yet to be discovered.

PROSPECTIVE RESOURCES. petroleum which is estimated to be potentially recoverable from undiscovered accumulations.

ESTIMATED ULTIMATE RECOVERY. those quantities of petroleum which are estimated to be potentially recoverable from an accumulation, plus those quantities already produced.

RANGE OF UNCERTAINTY. "Best Estimate" is considered to be the closest to the quantity that will actually be recovered from the accumulation between the date of the estimate and the time of abandonment. This is usually the most likely/mode, median/P50 or mean value of a probability distribution. The terms "Low Estimate" and "High Estimate" are typically the 90% and 10% probability estimates

All terms are dependent on the date the estimate is made.



Reference: <http://energy.cr.usgs.gov/OF98-34/ANWR1002.pdf>

In-place: Amount present without regard to recoverability or economics

Recoverable: Amount that can be recovered using current technology without regard to cost

Economically recoverable: Costs of discovery, development, production, and return on capital are less than a given well-head price.

The USGS geological assessments consider the probabilities of finding a certain amount of a resource. (In USGS analyses these probabilities are often expressed as fractions, called fractiles, similar to the more familiar academic term, percentiles, where the probabilities are represented in percents.) For a given amount of the resource, these number represent the probability that **at least** that amount of resource will be found.

Published reports typically report 5% and 95% probability amounts. When you ask how much oil (or any other resource) will you find with a 95% probability, the number will be small, because a 95% probability is almost a certainty. However, when you ask how much you will find with a 5% probability, the number will be quite large, because a 5% probability is close to an educated guess.

The USGS reports also give a mean value for the expected amount of the resource. This mean value is close to, but not the same as the 50% probability because the Monte Carlo simulations used in the calculations can produce a non-uniform probability distribution. (Only a uniform probability distribution, like the conventional normal distribution, has the mean value at the midpoint (50% point) of the distribution.)

Hubbert Peak

- Analysis due to M. King Hubbert
- Main publications in 1949 and 1956
- Correctly predicted peak in US oil production in early 1970s
- Not so accurate in other predictions
- Some recent applications show world oil production peak in next ten years
- Many other studies show later peak

Copies of original references:

M. King Hubbert, "Energy from Fossil Fuels," *Science* **109**:103-109, February 4, 1949. Copy found at <http://www.hubbertpeak.com/hubbert/science1949/> on January 27, 2007.

M> King Hubbert, "Nuclear Energy and the Fossil Fuels", paper presented at spring meeting of Southern District Division of Petroleum, American Petroleum Institute, March 7-8-9, 1956. Copy found at <http://www.hubbertpeak.com/hubbert/1956/1956.pdf> on January 27, 2007.

How well can one estimate the ultimately available resource, Q_{∞} ?

Symmetric curve approach ignores many factors: economic, political, technological

Suggested approach is use of separate curves for each production area and aggregation of such curves

References (all web sites accessed January 28, 2007)

[http://www.gasresources.net/Lynch\(Hubbert-Deffeyes\).htm#_ftn1](http://www.gasresources.net/Lynch(Hubbert-Deffeyes).htm#_ftn1) points out flaws in main proponents of Hubbert analysis

<http://dieoff.org/page191.htm>: The article by J.H. Laherrère discusses details of approaches to Hubbert analysis and restrictions in the assumptions that should be applied. The article endorses the use of multiple curves in consistent regions to model world production

<http://www.princeton.edu/hubbert/>: The web site of Kenneth S. Deffeyes, author of the book *Beyond Oil*, who forecasts a peak in world oil production in 2005.

In 2005 the National Academies had a conference to discuss various different opinions on the oil peak. The proceedings of that conference were published as **Trends in Oil Supply and Demand, Potential for Peaking of Conventional Oil Production, and Possible Mitigation Options: A Summary Report of the Workshop**, James Zucchetto, Editor, Planning Group for the Workshop on Trends in Oil Supply and Demand and the Potential for Peaking of Conventional Oil Production, National Research Council of the National Academies, 2006. The report may be downloaded at: <http://www.nap.edu/catalog/11585.html>.

The conference summary presents all the divergent views, but does not try to reconcile them

World Energy Resource ~1999

Fuel	Exajoules
Coal	290,000
Petroleum	2,600
Natural Gas	5,400
Tar Sands	5,700
Oil Shale	11,000
Peat	3,000
Uranium (^{235}U)	2,600

- Total is 320,000 EJ
- quad/EJ = .96
- 2005 world energy use is 443 quads
 - Forecast growth rate is 1.775% per year

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Taken from Table 7.2 on page 303 of the course text by Tester *et al.* There is no reference for these data, but the date for the data is given as “around 1999”.

This shows that there is a tremendous energy resource in coal, but the smallest resource is in petroleum, conventional oil. Both coal and oil shale have significant environmental problems compared to other fuels.

The uranium resource is the same as oil in this chart, but that assumes that none of the uranium is used in reactors that can create more nuclear fuel. Such reactors, known as breeder reactions, will be discussed later in the course. They are designed to operate at such conditions that the nuclear reactions, in addition to providing heat to generate electricity, will produce additional nuclear isotopes that can be used as reactor fuel.

Renewable resources include solar and wind. Solar has the potential to supply all our energy needs. Potential resource that will not probably be developed for 30 to 50 years is gas hydrates.

There are 36,729 Btu/ft² in one kWh/m². The annual US energy use is about 100 quads or 10¹⁷ Btu/year; this is an average of 10¹⁷/365 Btu/day = 2.74x10¹⁴ Btu/day. An annual average solar radiation of 4 kWh/m²/day is equivalent to 1.465x10⁵ Btu/ft²/day. At this rate the annual average US energy use could be supplied by an area of (2.74x10¹⁴ Btu/day) / (1.465x10⁵ Btu/ft²/day) = 1.865x10⁹ ft² = 66.9 mi². Assuming an overall efficiency of 20% for conversion of solar energy into the eventual energy use would require an area of 335 mi². Different assumptions for the annual average energy flux and the efficiency would yield different areas. One often sees the figure of 400 mi² to supply the total energy needs of the US. This can be compared to the land area of Arizona, a good area for solar energy, which is 113,642 mi².

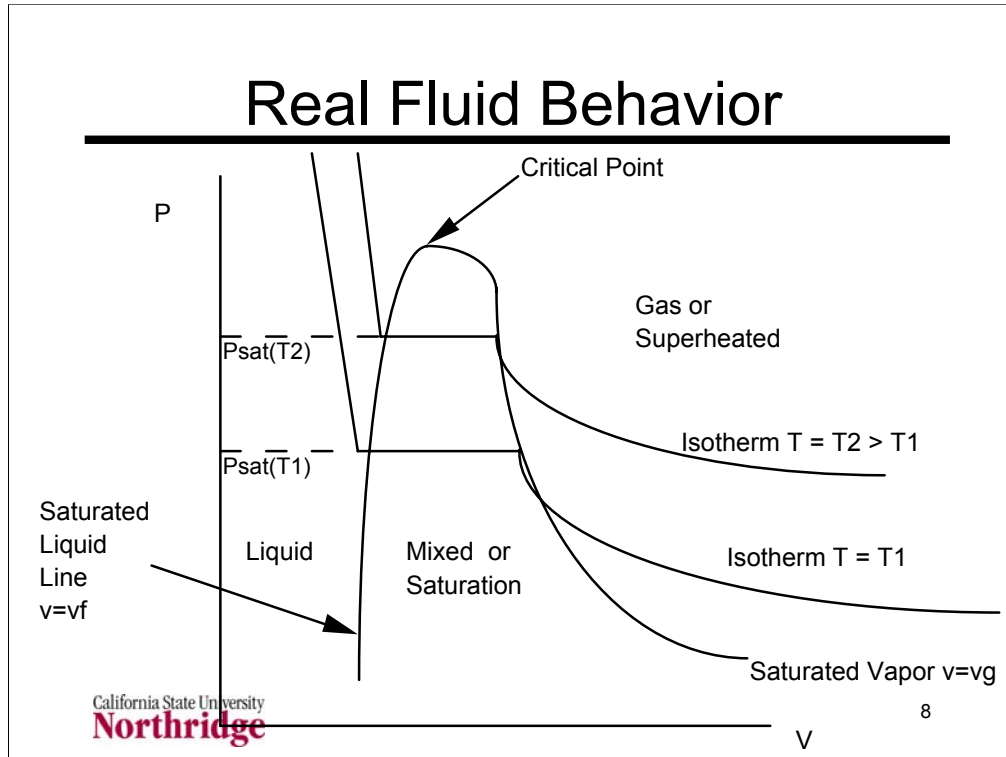
Thermodynamic Properties

- Ideal gas law
 - $PV = mRT$
 - $Pv = RT$
 - $P = \rho RT$
- Can also use molar units
- Pure substances have gas, liquid and mixed region. (Also have triple point and solid-vapor behavior)

The simplest property relations are for ideal gases. In engineering calculations we use the engineering gas constant, R , which is different for each species. The universal gas constant, $R_u = 8.31557 \text{ kJ/kgmol}\cdot\text{K} = R_u = 8.31557 \text{ kPa}\cdot\text{m}^3/\text{kgmol}\cdot\text{K} = 10.7316 \text{ psia}\cdot\text{ft}^3/\text{lbmol}\cdot\text{R} = 1.98588 \text{ Btu/lbmol}\cdot\text{R}$. M is the molar mass. The engineering gas constant, defined by the equation $R = R_u/M$, can be found in tables or computed from the universal gas constant and the molar mass of the substance you are using.

Ideal gas relations apply at pressures that are low compared to the critical pressure and at temperatures that are high compared to the critical pressure. Combustion conditions can usually be modeled quite well by ideal gas relations; this is even true for internal combustion engines where the operating pressures can be several times atmospheric pressure.

When considering ideal gas mixtures, the engineering gas constant is simply the weighted average (using mass fractions) of the gas constants for each species in the mixture. Alternatively it may be computed as the universal gas constant divided by the mean molecular weight of the mixture.



Thermodynamic tables (or computer programs) can be used to find property data for pure substances in both the mixed and one-phase regions.

Mixed region properties are based on mass fraction of vapor, called the quality x . The mixed region is a mixture of different proportions of the vapor about to condense (saturated vapor) with the v subscript and the liquid about to evaporate (saturated liquid) with the f subscript. These properties are functions of either temperature or pressure which are related for the mixed region.

$$v(x, T) = v_f(T) + xv_{fg}(T)$$

$$v(x, P) = v_f(P) + xv_{fg}(P).$$

Extensive thermodynamic variables depend on the size of the system; these include volume, V , internal energy, U , enthalpy, H , entropy, S , Helmholtz function, $A = U - TS$, and the Gibbs function, $G = H - TS$

Intensive variables such as the temperature, T , and the pressure, P do not depend on the size of the system.

Specific properties are intensive properties that are the ratio of an extensive property to the mass of the system. These include specific volume, $v = V / m$, specific enthalpy, $h = H / m$, specific entropy, $s = S / m$, specific Helmholtz function $a = A / m$, and specific Gibbs function, $g = G / m$.

We can also write properties on a per unit mole basis.

State of a thermodynamic system is known when two of its properties are specified. We can then find all properties for the system (provided that we have the necessary data.) For simple systems, two variables are sufficient to satisfy the state of the system. For complex systems with C components and P phases the Gibbs phase rule gives the number of independent variables, called the degrees of freedom: $F = C - P + 2$. degrees of freedom.

Work and Paths

- The work done by a closed system on its surrounding during a process is found as $\int_{\text{path}} P dV$
 - this is the area under the path when it is plotted on a P-V diagram.
- Quasi-static processes assumed
 - No significant departures from equilibrium such as a shock wave of the rupture of a membrane between two pressures

The basic analysis unit is called the system. We analyze interactions at boundary between a system and it's surroundings

Closed systems have fixed mass; open systems exchange mass with surroundings. Closed systems can change in volume.

Isolated system has no interchange of energy of mass with surroundings. Subsystems of an isolated system can change volume, but the overall volume of an isolated system is constant.

Thermodynamics deals with equilibrium states. In theory there can be no processes analyzed by thermodynamics. However, one uses the idealization of a quasi-static process in which the changes in properties are assumed to be slow compared to the underlying physical processes. For example, moving a piston changes the pressure slowly compared to the time for a pressure wave to travel across the cylinder making the assumption of a quasi-static process appropriate for analysis of piston movement, even in high RPM engines.

The path is the sequence of equilibrium that the process follows from its initial state to its final state. Paths may be simple ones such as constant pressure for which the work is $P\Delta V$ or constant volume for which the work is zero. More complex paths can also be used. An empirical formulation is known as the polytropic path $PV^n = C$, a constant. In this path n is an empirical constant. For this path between an initial state (1) and a final state (2) the work is given by the equation $W = (P_2V_2 - P_1V_1)/(1-n)$.

Heat and the First Law

- Heat, Q , is energy in transit due only to a temperature gradient
- Heat added to a system is positive; heat rejected from a system is negative
- Work, W , done by a system is positive; work done on a system is negative
- $u = U/m =$ internal energy is a property
- Closed system: $Q = \Delta U + W = m\Delta u + W$

The analysis for closed systems is done for some unstated time period. During this period (at some duration so that we can say that the process is quasi-static) a certain amount of heat is added and a certain amount of work is done. Units for heat and work are typically Btu or kJ. The ΔU term is the product of the system mass, m , and the specific internal energy, u . The value of u can be found from property tables for real substances.

For ideal gases the specific internal energy is a function of temperature only; i.e., $u = u(T)$ for ideal gases. In particular, $du = c_v dT$, where c_v is the constant volume heat capacity. For small temperatures differences we can assume that c_v is constant. For larger temperatures differences we have to integrate an expression for $c_v(T)$. Ideal gas tables provided such integrals.

Although work is usually found as $\int_{\text{path}} P dV$ there are other ways in which we can provide work. For example a mechanical paddle wheel or electric current crossing the system boundary provide work.

Open System First Law

- For an open system (control volume) with numerous inlets and outlets

$$\frac{dE_{cv}}{dt} = \dot{Q} - \dot{W}_U + \sum_{inlets} \dot{m}_{inlet} \left(h_{inlet} + \frac{\vec{V}_{inlet}^2}{2} + gz_{inlet} \right) - \sum_{outlets} \dot{m}_{outlet} \left(h_{outlet} + \frac{\vec{V}_{outlet}^2}{2} + gz_{outlet} \right)$$

$$q = \frac{\dot{Q}}{\dot{m}}$$

$$w_u = \frac{\dot{W}_u}{\dot{m}}$$

- Note that this is a rate equation \dot{Q} , \dot{W}_u , and \dot{m} are, respectively the heat rate, useful work rate, and mass flow rate and \vec{V} = velocity

Open systems are much more common than closed systems in practical engineering energy systems. (The analysis of a reciprocating internal combustion engine is the main application of closed system analysis.) Even what you might think of as a closed system, such as your home refrigerator can best be analyzed as a collection of open systems.

The energy term, E_{cv} , is the mass inside the control volume times the following specific energies: The work term W_u is called the useful work to distinguish it from the flow work that arises from pumping fluid into and out of the system. (This flow work, equal to the Pv product, is added to the internal energy of the entering flow. The combination $u + Pv$ is called the enthalpy. The enthalpy in the inlet and outlet flow terms then represents the sum of the internal energy and flow work.

The general equation written above can be written in many different forms for various simplifications. The easiest case of all is a steady system for which $dE/dt = 0$ having only one inlet and one outlet. For such a system the first law can be written as follows:

$$q = h_{out} - h_{in} + w_u$$

Here q and w_u are the ratios of the heat rate and the useful work rate, respectively, to the mass flow rate. For the steady flow case there is only one mass flow rate. (See next slide.)

Open System Mass Balance

- For open systems mass is conserved

$$\frac{dm_{cv}}{dt} = \sum_{inlets} \dot{m}_{inlet} - \sum_{outlets} \dot{m}_{outlet} \quad \dot{m} = \rho \vec{V}A = \vec{V}A / v$$

- For steady systems

$$\frac{dm_{cv}}{dt} = 0 \quad \Rightarrow \quad \sum_{inlets} \dot{m}_{inlet} - \sum_{outlets} \dot{m}_{outlet}$$

- If only one inlet and one outlet

$$\dot{m}_{inlet} = \dot{m}_{outlet} = \dot{m}$$

The equation relating mass flow rate, density (or specific volume), velocity, and cross sectional area is a fundamental relation among these variables. This is sometimes called the continuity equation. It applies to both steady and unsteady systems.

Many energy producing and absorbing systems can be treated as steady systems. Even if the load is varying, the time required for transients is small compared to the time that the system operates at a steady state. Such systems are called quasi-steady.

For example, a home furnace or home air conditioner operates with a controller that typically operates in an on-off fashion. The transient period of start-up and shut-down is usually very small compared to the time that the device operates. Thus the actual operation can be considered to be a steady process.

Ideal Gas Energy Properties

- The internal energy of an ideal gas depends on temperature only
 - Defined in terms of heat capacities

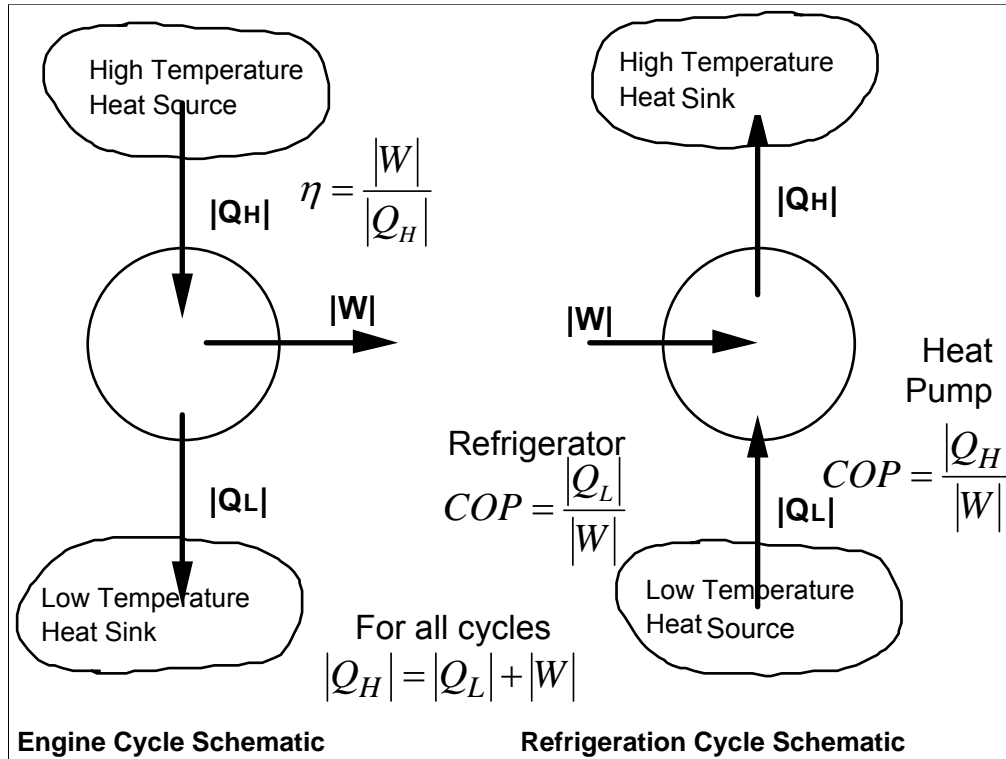
$$c_v = \left(\frac{\partial u}{\partial T} \right)_v \quad c_p = \left(\frac{\partial h}{\partial T} \right)_p$$
 - $du = c_v(T)dT$ and $dh = c_p(T) dT$ regardless of process
 - For small ΔT , assume c_v, c_p constant
 - Can integrate or use tables otherwise

The heat capacity, c_x is defined as the ratio of heat transfer to temperature difference in a constant X process: $dQ = c_x dT$. However, the heat capacities are properties of the substance and do not depend on the process. From basic property relations for any substance, it is possible to show that $du = c_v dT$ and $dh = c_p dT$ for the ideal gas. This holds for any process.

From the definition of enthalpy as $h = u + Pv$ we that $h = u + RT$ for an ideal gas.

Differentiating this equation gives $dh = du + RdT$ so that $c_p dT = c_v dT + RdT$ and division by dT gives the following result for the ideal gas: $c_p = c_v + R$.

The ratio of heat capacities, c_p/c_v occurs in various processes and is given the symbol k or γ , depending on the author. The symbol γ is more commonly used in publications in chemistry, physics, and aerospace engineering. The term k is more commonly used in mechanical engineering.



Cycles are a fundamental concept in energy production and use.

In an engine cycle the device gets heat $|Q_H|$ from a high temperature source, performs a certain amount of work, $|W|$, then rejects heat $|Q_L|$ to a low temperature sink.

In a refrigeration cycle the device gets heat $|Q_L|$ from a low temperature source, has an input of a certain amount of work, $|W|$, then rejects heat $|Q_H|$ to a high temperature sink. In your home refrigerator the low temperature source is as the inside of the refrigerator. Work is done by an electric motor and the high temperature heat transfer is done by the coils in the back of the refrigerator.

The refrigeration cycle is used in two ways. The conventional way is to remove heat from a low-temperature source to cool that source. The other way, called a heat pump, is to provide energy at high temperature. This is done by cooling the outdoors. Although this seems unusual at first, it is an advantage when the alternative for heating is electric resistance heating.

Note that traditional cycle analysis does not use the usual sign conventions for heat and work; instead it uses quantities that are always positive (denoted here by absolute value signs.) For both the engine and refrigeration cycles we can write $|Q_H| = |Q_L| + |W|$.

Cycle problems

- A power plant with an output of 460 MW has an efficiency of 39%. What is its heat input and heat rejection in Btu/h?
- A refrigeration cycle has a COP of 2 when operated as a refrigerator. What is its COP as a heat pump?
- Engine cycle $\eta = |W|/|Q_H|$
- $\text{COP}_{\text{ref}} = |Q_L|/|W|$ $\text{COP}_{\text{hp}} = |Q_H|/|W|$
- $|Q_H| = |Q_L| + |W|$ for cycles

$$3412 \text{ Btu} \\ = 1 \text{ kWh}$$

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We can apply the efficiency equation to the work rate (power) and the heat input rate. This gives $|Q_H| = |W| / \eta = (460 \text{ MW}) / 39\% = 1179 \text{ MW}$
 $|Q_H| = (1179 \text{ MW})(1000 \text{ kW/MW})(3412 \text{ Btu/kWh}) = 4.025 \times 10^9 \text{ Btu/h}$
 $|Q_L| = |Q_H| - |W| = 4.025 \times 10^9 \text{ Btu/h} - (460 \text{ MW})(1000 \text{ kW/MW})(3412 \text{ Btu/kWh}) = 2.455 \times 10^9 \text{ Btu/h}$

If we assume that the operating conditions are the same for both the refrigeration and heat-pump cycle we can use the cycle heat balance and the definition of the COP terms as follows:

$$|Q_H| = |Q_L| + |W|$$

$$|W|\text{COP}_{\text{HP}} = |W|\text{COP}_{\text{REF}} + |W|$$

Dividing by $|W|$ gives $\text{COP}_{\text{HP}} = \text{COP}_{\text{REF}} + 1$

So the COP of the cycle for the heat pump is the COP of the cycle as a refrigerator plus 1

Carnot Cycle

- Ideal cycle between two and only two temperatures: T_H and T_L
- Highest efficiency (and COP) of any cycle (with only two temperatures)
 - Mainly of theoretical interest but predicts correct trends for real cycles

$$\eta_{\text{Carnot}} = 1 - \frac{T_L}{T_H} \qquad COP_{\text{Carnot Refrigerator}} = \frac{T_L}{T_H - T_L}$$

$$COP_{\text{Carnot Heat Pump}} = \frac{T_H}{T_H - T_L}$$

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The Carnot cycle is mainly of theoretical interest because of its simple equations for efficiency and coefficient of performance. It played an important role in the original development of the second law in the first half of the 19th century. Practical implementations of a Carnot and physically difficult and the potential efficiency increase is not worth the extra cost.

The important qualitative results that the efficiency and COP equations show holds true for practical cycles. For an engine cycle you can increase the efficiency by making the low temperature heat sink have a lower temperature or making the high temperature heat source have a higher temperature. For a refrigeration cycle we can get a higher coefficient of performance by making the low temperature higher or by making the difference between T_H and T_L smaller.

Continued from previous page:

An engine cycle is rated by its efficiency, η , the ratio of work output to heat input. For a refrigeration cycle we would like to remove as much heat as possible from the low temperature source while doing the least amount of work. Thus the figure of merit for a refrigeration or heat-pump cycle, called the coefficient of performance, COP, is the ratio of the desired heat effect (removing $|Q_L|$ or providing $|Q_H|$) to the work input.

The efficiency of an engine cycle is between zero and one. The COP for a refrigeration or heat-pump cycle may be greater than one.

The notation $|q_H|$ and $|q_L|$ are used for heat transfer per unit mass.

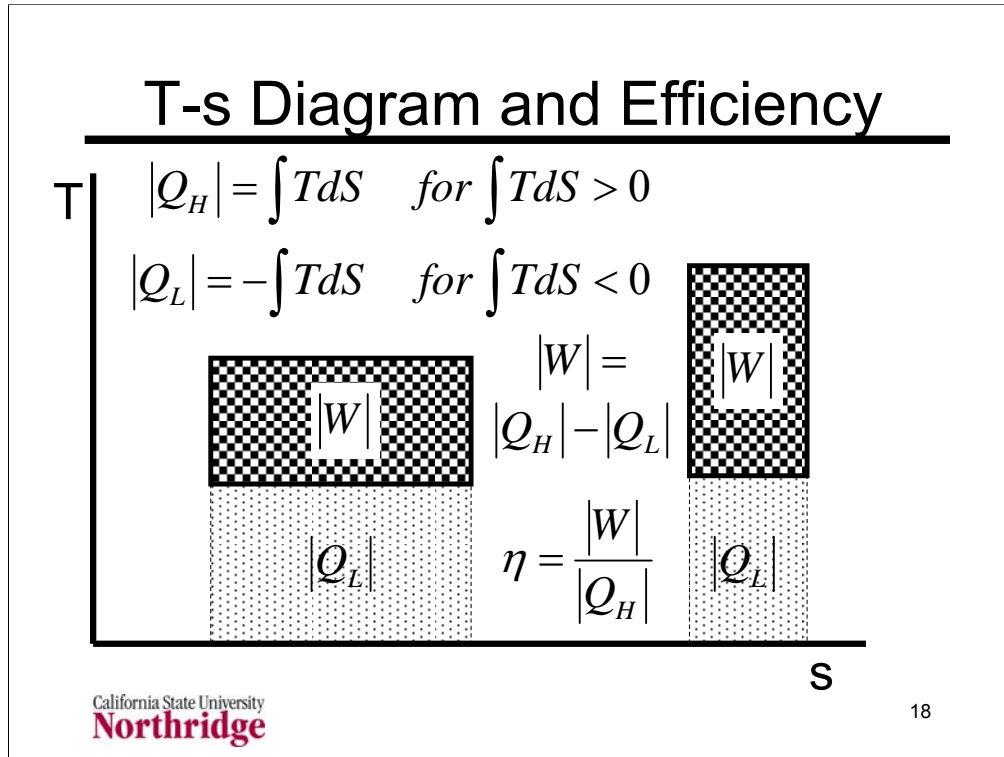
Second Law

- There exists an extensive thermodynamic property called the entropy (with the symbol, S) defined as follows:
- $dS = (dU + PdV)/T$
- For any process in a system $dS \geq dQ/T$, and, for an isolated system
- $\Delta S_{\text{isolated system}} \geq 0$
- **Impossible:** 100% efficient engine cycle and refrigeration cycle with $|W| = 0$

The second law provides a qualitative statement about limitations on cycles and it provides a mathematical tool, the entropy, to compute the efficiency of ideal cycles. We can use this tool, with the inequality relation that $dS \geq dQ/T$, to determine the ideal case as the case in which $dS = dQ/T$. This is known as the reversible cycle. The maximum efficiency occurs in a reversible cycle.

For reversible heat transfer, $dQ = TdS$ so that $Q = \int Tds$. If we can plot a reversible process on a diagram that has entropy as the abscissa and temperature as the ordinate (T-s coordinates or a T-s diagram) then the heat transfer is the area under the plot for that process.

No actual cycle is truly reversible, but we can try to approach reversibility as closely as possible within the constraints of cost. At some point the extra cost of making a device that is more nearly reversible outweighs the cost of the energy saved.



The temperature-entropy or T-s diagram is often used to plot cycles because it shows provides a visual way of comparing cycle efficiency, once you are familiar with the underlying relations.

Recall that for a reversible process $Q = \int TdS$. When we draw an ideal (reversible) cycle on a T-s diagram we can apply this equation. When the integral is positive, we have a heat input giving $|Q_H|$. When the integral is negative we have the heat rejected so that $|Q_L| = -\int TdS$. An engine cycle always operates in a clockwise manner. Each cycle can be viewed as starting in the upper left corner, then proceeding to the upper right corner and so on until the cycle is complete.

The chart uses the Carnot cycle, shown as the dark checked rectangles, as an example. There are only two parts of the cycle in which there is a heat transfer. Along the top part of the cycle, where the temperature is constant at a value T_H the integral gives $|Q_H| = T_H\Delta S$. The lower portion gives $|Q_L| = -(T_H)(-\Delta S) = T_L\Delta S$. The difference between $|Q_H|$ and $|Q_L|$ is the net cycle work, $|W|$.

The area corresponding to $|Q_H|$ is the sum of two different areas shown on the diagram: the dark checked area for the original cycle and the lower area. The lower area corresponds to $|Q_L|$. The difference between the two, which is the area in the cycle, is the work. The ratio of the cycle area to the total area (cycle area plus area beneath the cycle) is the efficiency.

Which of the two cycles has a greater efficiency?

Cycle Analysis

- The following assumptions define idealized versions of practical cycles
 - There are no line losses; the outlet state (i.e. thermodynamic properties) from one device is the same as the inlet state to the next device.
 - work devices are reversible and adiabatic so they have constant entropy (isentropic).
 - Heat transfer devices have no pressure loss and are reversible so $Q = \int T ds$
 - Outlet states from devices with two phases are saturated liquids or vapors.

These assumptions give the highest efficiency for a given set of cycle conditions. In practice they are not met and the degree to which they are not met gives the difference between the actual or maximum cycle efficiency and the actual cycle efficiency.

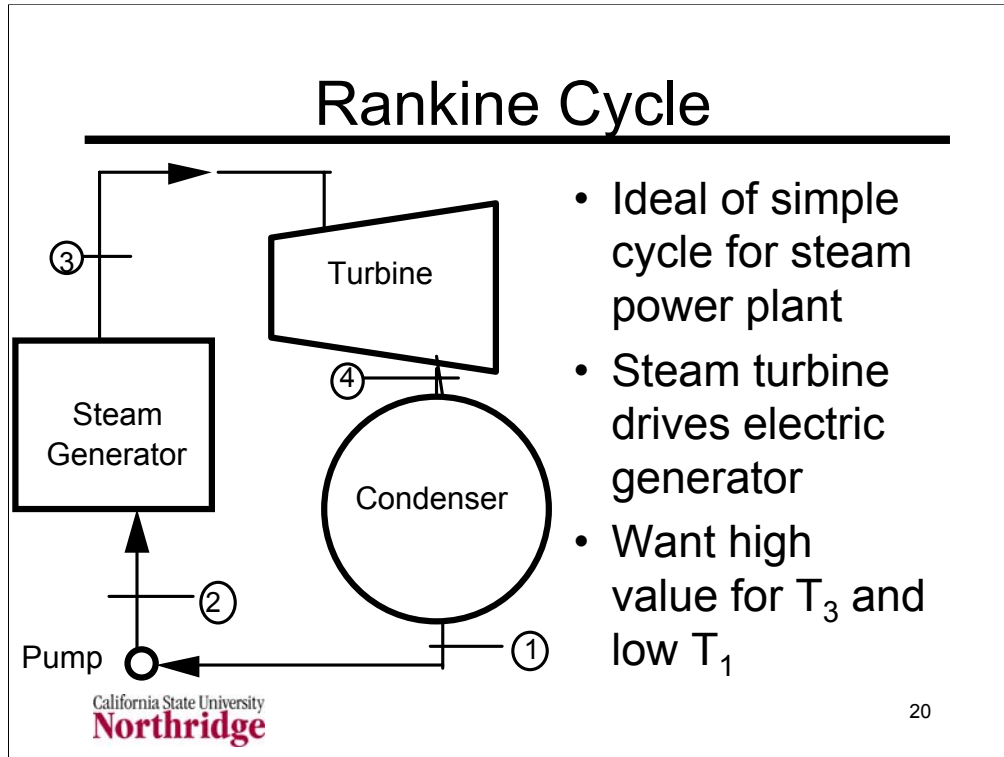
These assumptions can also be applied to the analysis of a refrigeration cycle to compute the maximum coefficient of performance.

The ideal (isentropic) work for pumping liquids is difficult to find in tables for two reasons. (1) Often compressed liquid tables are not available. (2) Even for water, where compressed liquid tables are available, the required interpolation leads to inaccuracies in the results.

As an alternative the following process is used. From the basic definition of entropy as $ds = (du + Pd v) / T$ and enthalpy as $h = u + Pv$ we can show that $dh = T ds + v dP$. For an isentropic process, $ds = 0$ and $dh = v dP$.

An ideal pump would be an isentropic device so we could apply $dh = v dP$ and get $\Delta h = \int v dP$ if we knew how v depended on P for an isentropic process. Fortunately, for a liquid, v is approximately constant so we can approximate Δh as $v \Delta P$. Typically this is applied in the following manner.

A pump is specified by an inlet state, from which all properties can be evaluated and an outlet pressure, P_{out} . From the inlet state we will know (or be able to find from property tables) h_{in} , P_{in} , and v_{in} . In terms of these variables, $\Delta h = v \Delta P$ for constant $v = v_{in}$ can be written as follows: $h_{out} - h_{in} = v_{in}(P_{out} - P_{in})$.



The application of the cycle idealizations to this simple Rankine cycle gives the following results. In this cycle heat is added in the steam generator and is rejected in the condenser. The net work output from the cycle is the difference between the work output from the turbine and the work input to the pump.

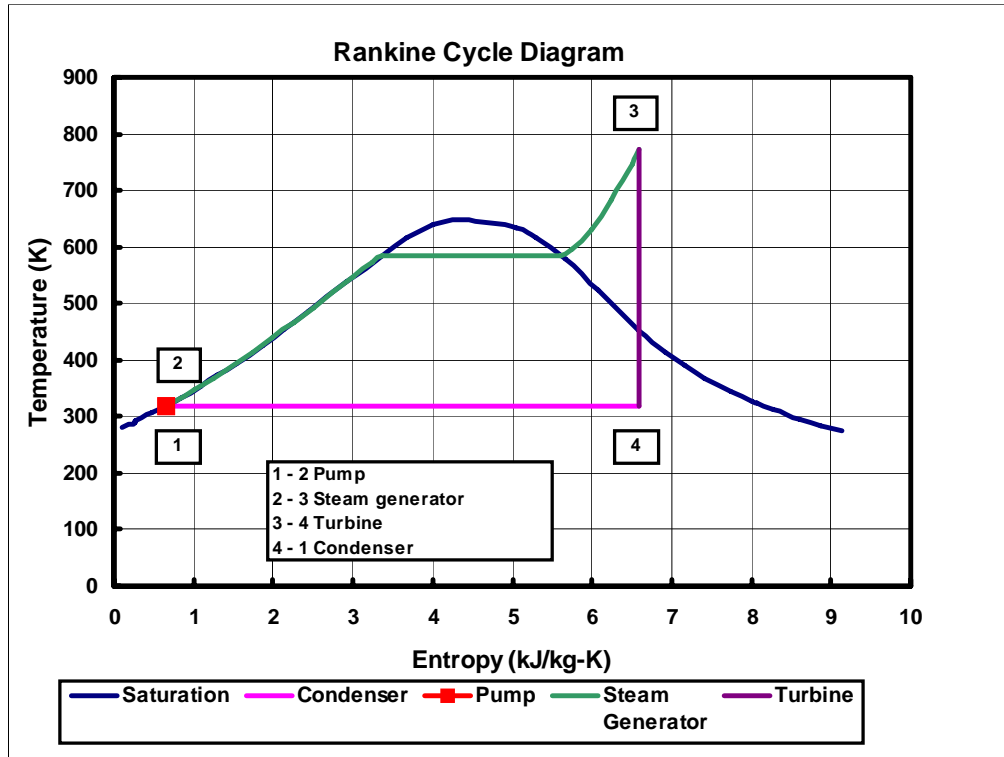
The assumption of **no line losses** is already included in the diagram. The four indicated points imply that there is no difference between the exit from one device and the entrance to the following device.

The assumption that **work devices are adiabatic and reversible** (which corresponds to an assumption that the process is isentropic or constant entropy) means that $s_2 = s_1$ and $s_4 = s_3$.

The assumption of **no pressure losses for heat transfer devices** gives the result that $P_4 = P_1$ and $P_3 = P_2$.

The assumption that the **exit from a two-phase device is saturated** means that the liquid exiting the condenser at point 1 is a saturated liquid.

The first law is applied to each device as a steady open system giving the work output from the turbine $h_3 - h_4$ and the work output from the pump as $h_2 - h_1$. (The equation for the pump uses the sign convention for work – input negative, output positive – to compute pump work “output”; this will be negative indicating that there is a work input here.) The heat transfer to the steam generator is $h_3 - h_2$ and the heat transfer to the condenser is $h_1 - h_4$. (As with the pump, the sign convention for heat gives a heat input as positive so the computed heat “input” for the condenser, where heat is removed to cool the water, will be negative.)

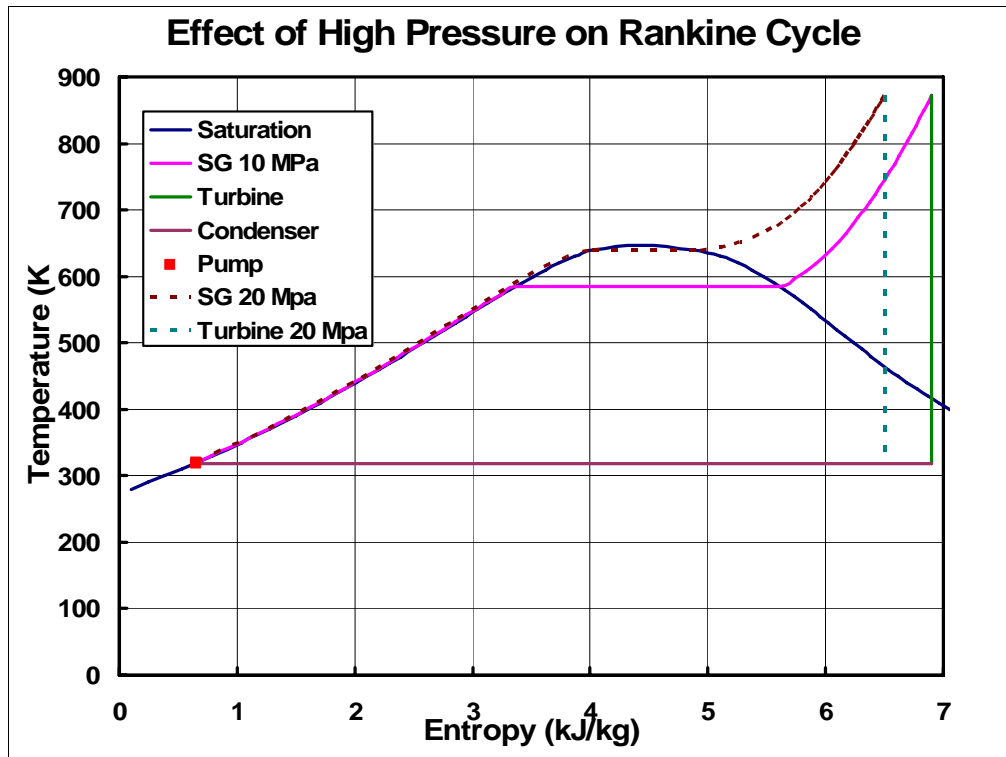


The state points for one particular example of a Rankine cycle (with a turbine inlet pressure and temperature of 10 MPa and 500°C and a condenser pressure of 10 kPa) is shown on this diagram. The temperature increase in the pump is so small that the difference between the inlet and exit does not show on this diagram.

The green line from point 2 to point 3 for the steam generator is actually a small amount above the saturated liquid line, but for the scale of this diagram the two lines appear to be identical. As noted previously the cycle idealization for heat transfer in the steam generator is a constant pressure process. We see that in the mixed region, the constant pressure gives a constant temperature. Outside this region the slope of a constant pressure line is positive. We can show that the slope of this line $(\partial T / \partial s)_P = T / c_p$.

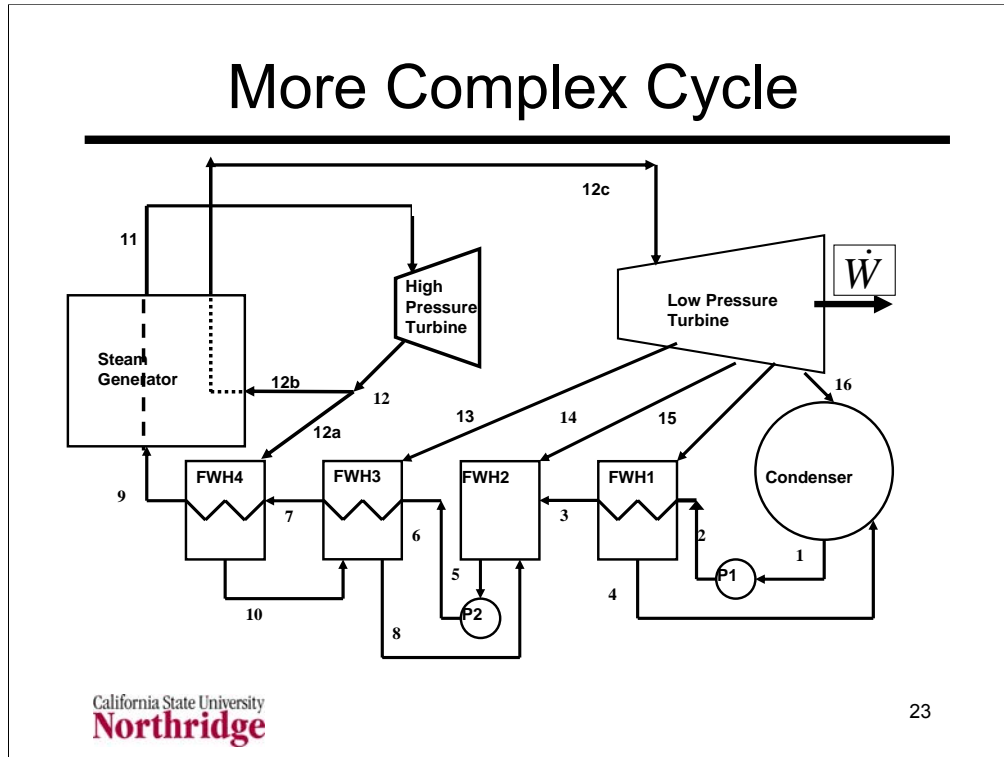
The isentropic (constant entropy) process in the turbine appears as a straight vertical line and the constant pressure in the condenser gives a straight horizontal line on the T-s diagram since the condenser fluid is always in the mixed region.

With the equations on the previous notes page for heat and work terms, the net work is the turbine output minus the pump input: $h_3 - h_4 + h_1 - h_2$. With this expression, the efficiency, η , which is the net work divided by the heat input is: $(h_3 - h_4 + h_1 - h_2) / (h_3 - h_2)$. Using the relationship for pump work gives $h_2 - h_1 = v_1(P_2 - P_1)$.



This chart shows the Rankine cycle from the previous chart and the changes that would be made if the Rankine cycle had a pressure of 20 MPa in the steam generator instead of 10 MPa as in the previous example. (The other defining variables remain the same.) The solid lines are for the original cycle; the dashed lines are for the cycle with a pressure of 20 MPa. (The condenser line for the revised cycle is concurrent with the condenser line for the original cycle; the pump work is double that of the original cycle, but the difference in temperature is still too small to show on this scale.)

A direct calculation shows that the efficiency increases from 41.7% to 43.8% when the steam generator pressure is increased from 10 to 20 MPa. It is not easy to compare the differences in the area of two cycles since there are places where the areas increase and places where they decrease. However, an accurate measurement of the areas of the two cycles would show that the higher pressure cycle has added work but reduced heat rejection resulting in a higher efficiency.



Although the previous example shows that increased pressure improves efficiency, the exit state from the turbine would have a larger fraction of liquid droplets that are dangerous for the turbine. In order to reduce the amount of liquid formation in the turbine, the steam from a high pressure turbine is reheated and introduced into the low pressure turbine stages. This does not improve efficiency, but it allows the use of increased temperatures and pressures that do increase efficiency. Such efficiency increases would not be possible without reheating.

An other approach to improving efficiency is to withdraw a small amount of steam at various temperatures to heat the water that is going to the steam generator. This water is called the feedwater and the devices where the turbine exhaust heats this feedwater are called feedwater heaters (denoted as FWH in the diagram above.) The diagram above shows one possible arrangement where there are four feedwater heaters. The second one (FWH2) is called an open feedwater heater because the turbine exhaust and the feed water mix. The others are closed feedwater heaters where the turbine exhaust transfers heat to the feed water and then exits to a feedwater heater with a lower pressure. (Not shown on the diagram are traps at points 4, 8, and 10 that reduce the pressure.)

As shown in the diagram, the reheating of steam between the high pressure and low pressure turbine (from 12b to 12c) is in the same unit as that used to heat the water initially.

Air Standard Cycle

- Idealization of cycles in combustion engines
 - Otto cycle: gasoline engine
 - Diesel cycle
 - Brayton cycle: gas turbine
- Model actual operation as cycle
 - Assume air as working fluid with heat addition to model combustion
 - Assume heat rejection in place of exhaust

In air standard cycle analysis the working fluid is treated as an ideal gas with constant or variable heat capacity. (The temperatures encountered in such analyses lead to a significant difference between the constant and variable heat capacity assumption.)

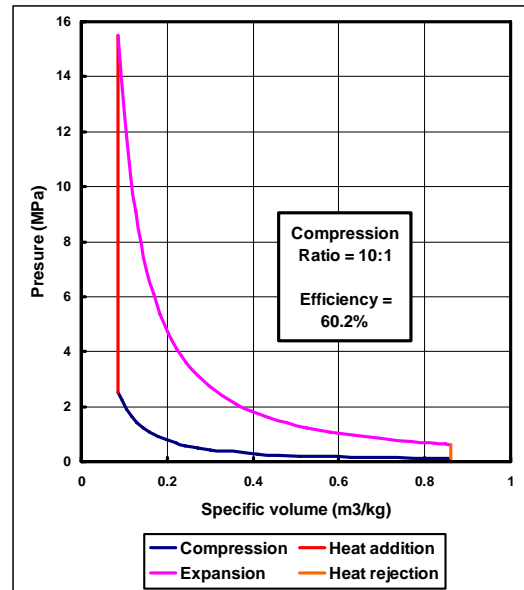
In an actual engine air (or an air-fuel) mixture is taken in to the engine, compressed and combustion takes place producing a gas at high temperature and pressure. This gas then expands producing power and is exhausted from the engine. In the air standard cycle the working fluid is assumed to be pure air – not as bad an approximation as it sounds since fuel/air mixtures typically have an air/fuel mass ratio of about 15:1. Instead of modeling the combustion process, there is an assumed heat addition step to produce an end state similar to that of the combustion process. Following the expansion process the air in the theoretical cycle is assumed to be cooled to the intake state and the cycle resumes.

For reciprocating engines such as those used in cars and trucks an important design parameter is the compression ratio, CR, the ratio of the maximum cylinder volume to the minimum cylinder volume. For the Otto cycle with a constant heat capacity the air-standard cycle predicts that the cycle efficiency, $\eta = 1 - 1 / (CR)^{1-k}$, where $k = c_p / c_v$ is the heat capacity ratio. This increase in efficiency with an increase in compression ratio is found in practice.

Otto Cycle

- **Given:** CR, P_1 , T_1 , q_H
- $v_1 = RT_1/P_1$
- $v_2 = v_1/CR$
- Isentropic compression to P_2
- $P_2 = P_1(CR)^k$
- $T_2 = P_2 v_2/R$

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This chart shows the diagram of an Otto cycle, the idealization of the cycle in a gasoline engine. It also shows the start of the cycle analysis. The compression and expansion are assumed to be adiabatic. The only heat transfer in the cycle is the constant volume heat addition and rejection. The remainder of the analysis is shown below.

The very high efficiency of 60.2% shown for a compression ratio of 10:1 is quite unrealistic, however the efficiency equation from the previous page does predict the observed trend that efficiency increases with compression ratio.

Remainder of analysis:

2 – 3 Constant volume heat addition: $T_3 = T_2 + q_H/c_v$, $v_3 = v_2$, and $P_3 = RT_3/v_3$

3 – 4 Isentropic expansion: $v_4 = v_1$, $P_4 = P_3/(CR)^k$, and $T_3 = P_3 v_3/R$

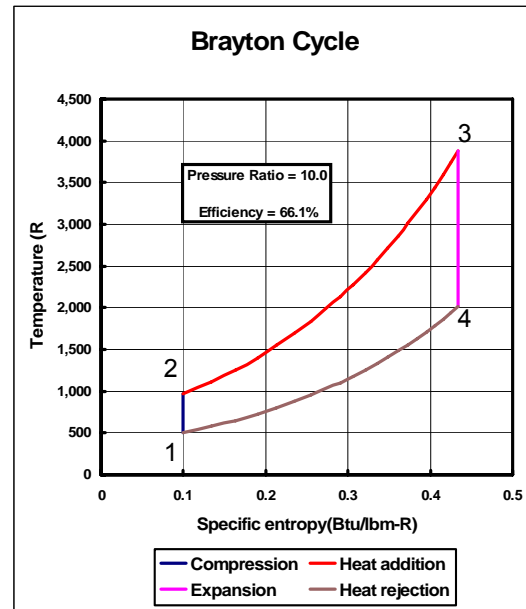
4 – 1 Constant volume heat rejection: $|q_L| = c_v(T_4 - T_1)$, $v_4 = v_1$, and $P_3 = RT_3/v_3$

Efficiency $\eta = 1 - |q_L|/q_H = 1 - c_v(T_4 - T_1)/[c_v(T_3 - T_2)] = (T_4 - T_1) / [T_4(CR)^{k-1} - T_1(CR)^{k-1}] = 1 - 1/(CR)^{k-1}$

Brayton Cycle

- Model of gas turbine engine
- Isentropic compression and expansion
- Constant pressure heat transfers

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The Brayton cycle shown here uses the typical idealizations of the air standard cycle. Air is the working fluid. Combustion is modeled as a heat addition and the exhaust process is modeled as a heat rejection. The analysis of this cycle is similar to that of the Otto cycle, except that the heat additions take place at constant pressure so that $q = \Delta h = c_p \Delta T$.

$$1 - 2 \text{ Isentropic compression in compressor: } T_2 = T_1(P_2/P_1)^{(k-1)/k}$$

$$2 - 3 \text{ Constant pressure heat addition: } T_3 = T_2 + q_H/c_p$$

$$3 - 4 \text{ Isentropic expansion in turbine: } T_4 = T_3(P_4/P_3)^{(k-1)/k}$$

$$4 - 1 \text{ Constant pressure heat rejection: } |q_L| = c_p(T_4 - T_1)$$

The pressure ratio across the compressor, P_2/P_1 is the same as the pressure ratio across the turbine, P_3/P_4 . Calling both these ratios the pressure ratio, PR, allows us to find the efficiency using the same approach used for the Otto cycle.

$$\text{Efficiency } \eta = 1 - |q_L|/q_H = 1 - c_p(T_4 - T_1)/[c_p(T_3 - T_2)]$$

$$= (T_4 - T_1) / [T_4(PR)^{(k-1)/k} - T_1(PR)^{(k-1)/k}] = 1 - 1/(PR)^{(k-1)/k}$$

Aircraft engines use only enough turbine work to run the compressor, the remaining energy is used to provide thrust. However, because of the similarities in design, General Electric is a major manufacturer of aircraft engines and of Brayton cycle (gas turbine) engines used for electric power production.

Combinations

- Combined cycle plants – use waste heat from one cycle as heat input to second (“bottoming”) cycle
 - Current applications: gas turbine waste heat used to power Rankine cycle
- Combined heat and power (CHP, previously called cogeneration)
 - Heat rejection is used to provide required process heat input

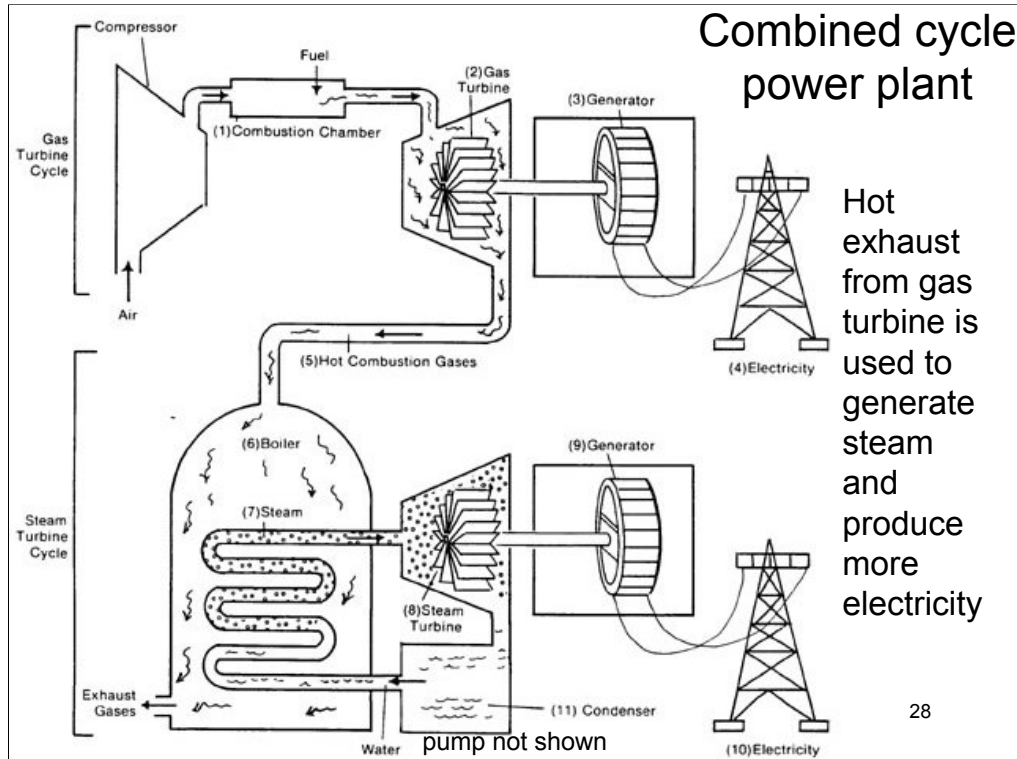
A diagram of a combined cycle plant is shown on the next chart.

Combined heat and power has a long history, but fell into disuse during the mid 20th century. After the oil price shocks of 1973 and 1979, it gained favor again. Part of the reason for the disuse was that central electric power plants were located far from potential uses of waste heat. Individual generators were discouraged by the pricing structure set by the utilities for power repurchase. This, individual companies who could use combined heat and power were limited in the power that they could generate because they could not sell excess power to the utilities at a reasonable price. Thus, systems were sized to the required electric power for the facility. Typically a facility’s heat demand could be met by CHP only if they generated more electricity than they consumed.

The Public Utilities Regulatory Policy Act of 1978 (PURPA) required regulated utilities to pay the avoided cost of building new power plants to independent power producers (IPP). This started a new wave of power plants built by third parties, the IPPs, who sold the electricity to a utility and sold the heat to a local industrial facility.

CHP remains an important energy conservation application today. The USEPA has published a Catalog of CHP Technologies that is available as a pdf file (accessed January 26, 2008):

http://www.gepower.com/prod_serv/products/gas_turbines_cc/en/h_system/index.htm



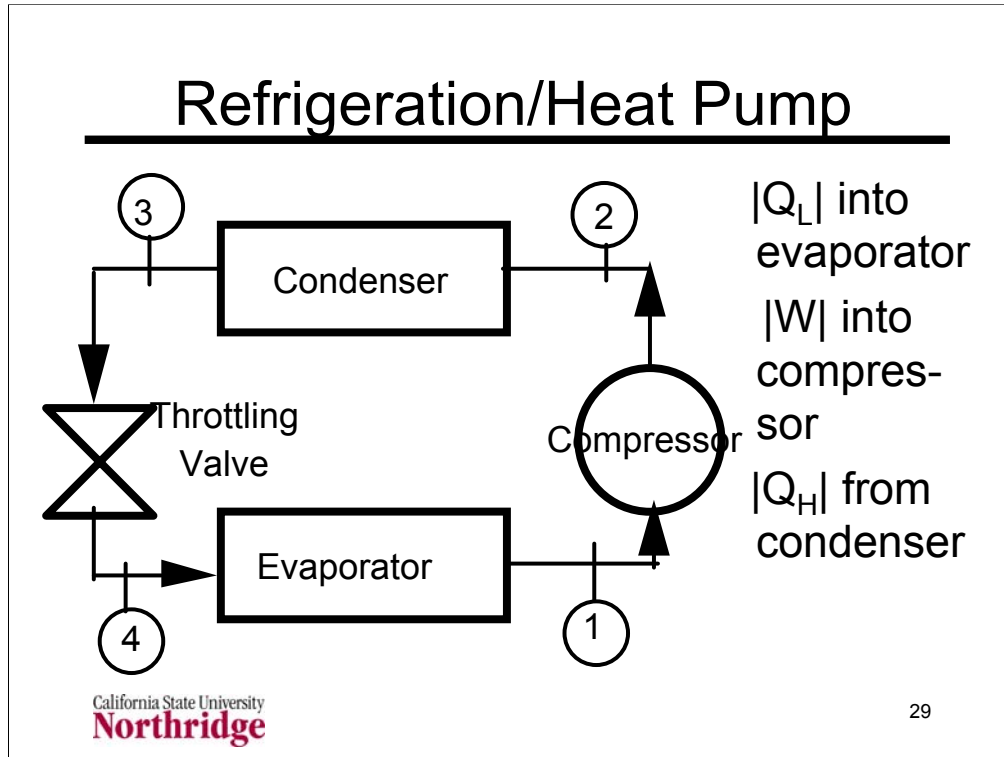
Reference: <http://www.eas.asu.edu/~holbert/eee463/combcycl.jpg>

The combined cycle power plant uses a gas turbine as the first stage to produce electric power. The high temperature exhaust gases from the turbine are then used in a heat-recovery steam generator (HRSG) to provide the heat required to produce steam for a Rankine cycle. The efficiency of the overall combined cycle plant is the net power output of both electrical generators (minus the work inputs) divided by the heat input into the gas turbine cycle.

Such power plants, using natural gas as the fuel, are now the choice for both high efficiency and clean operation.

A variation on the process shown above uses the exhaust gas from the turbine, which has a high oxygen concentration (about 15% molar) as the oxidizer for additional fuel. In this case the additional fuel represents an additional heat input and usually produces a lower efficiency for the cycle. However, it provides more power from the combined plant. (It also allows more control over power levels.)

General Electric, the largest provider of combined cycle plants, has achieved an efficiency of 60% for their H-System plant. See the GE web site at http://www.gepower.com/prod_serv/products/gas_turbines_cc/en/h_system/index.htm



The simple refrigeration cycle shown here is characterized by an evaporator pressure, P_{evap} , and a condenser pressure P_{cond} that is higher than the evaporator pressure. The compressor is assumed to be isentropic and the throttling valve adds no heat or work so the enthalpy change across the valve is zero.

The same cycle is used to model a heat pump for home heating. The only difference is that in the heat pump the interest is in the amount of heat transferred from the condenser to the inside of the house, $|Q_H|$.

Treating each device in this system as an open system gives the following equations for the components:

$$\text{Compressor: } s_2 = s_1, |w| = h_2 - h_1$$

$$\text{Evaporator: } |q_L| = h_4 - h_1 = h_3 - h_1$$

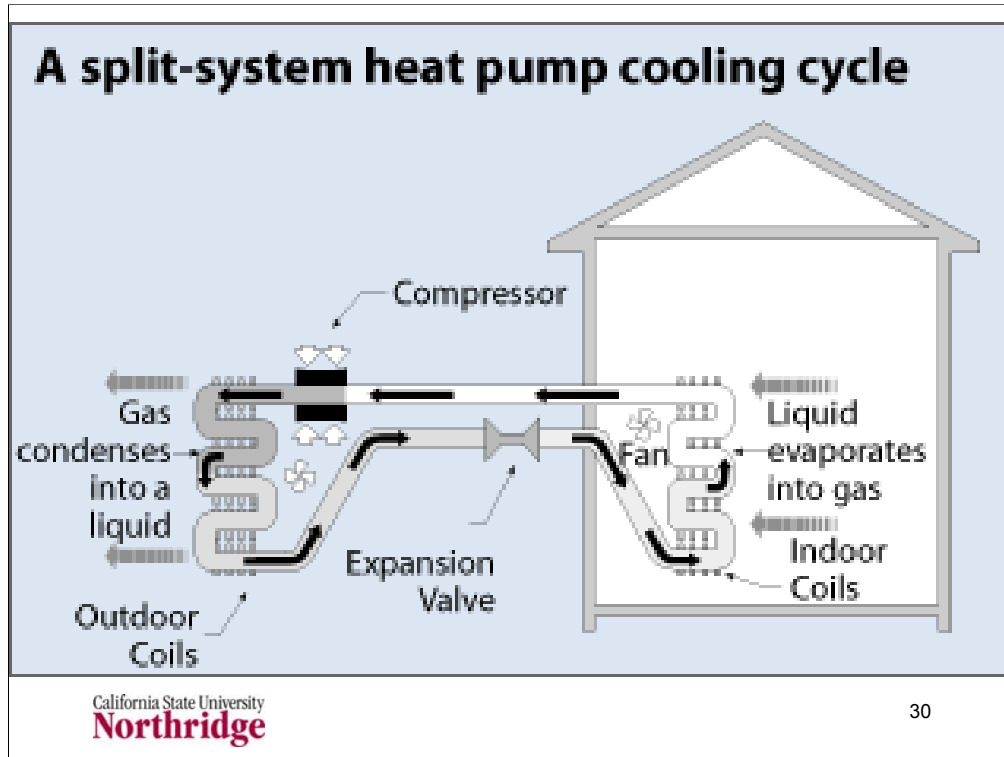
Refrigeration cycle coefficient of Performance:

$$\text{COP}_{\text{refrigeration}} = |q_L|/|w| = (h_4 - h_1) / (h_2 - h_1)$$

Heat pump cycle coefficient of Performance:

$$\text{COP}_{\text{refrigeration}} = |q_H|/|w| = (h_2 - h_3) / (h_2 - h_1)$$

For large differences in temperature between the evaporator and condenser a staged refrigeration cycle can be used to improve the coefficient of performance. In some cases an expander can be used in place of the throttling valve to produce work while reducing the pressure. This is only done when there is very large pressure difference such as in gas liquefaction plants.



Taken from DOE web site on heat pumps (accessed January 27, 2008):
http://www.eere.energy.gov/consumer/your_home/space_heating_cooling/index.cfm/mytopic=12620

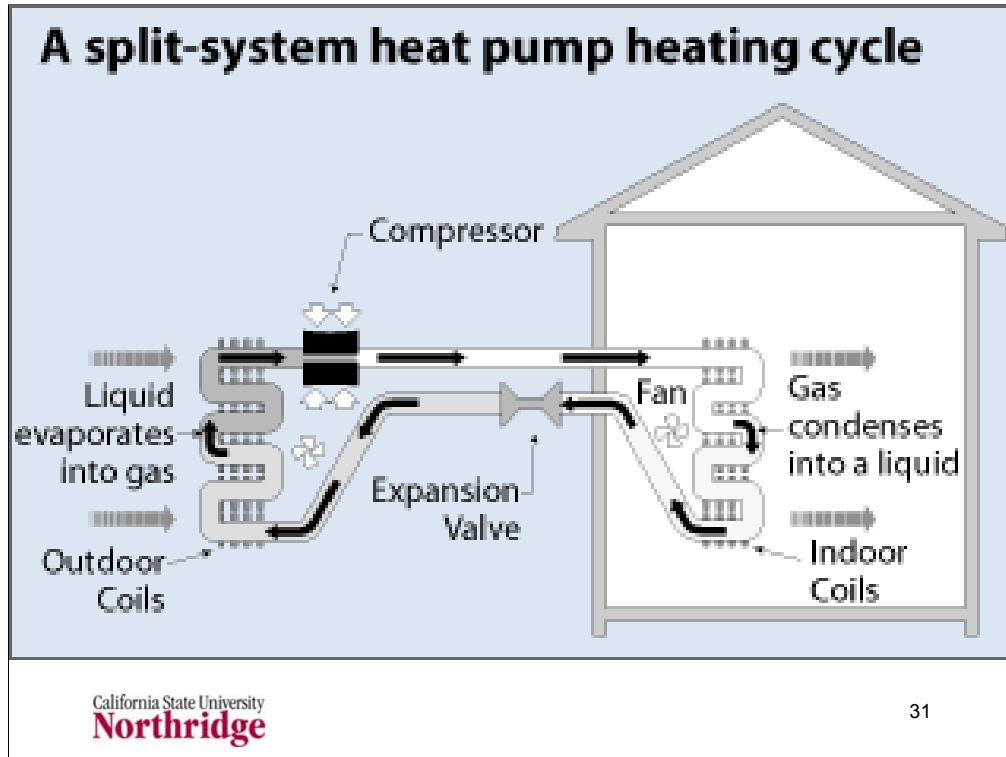
By appropriate changes in plumbing heat pumps can be used to either cool or heat the house. This chart shows the operation of the heat pump in the cooling mode. Here the evaporator (where the refrigerant evaporates to remove heat) is located inside the house. The condenser (where the refrigerant condenses rejecting heat) is located outside the house.

The measure of performance for heat pump operation during cooling is called the seasonal energy efficiency ratio (SEER). This is the like a coefficient of performance, except that the numerator and denominator are measured in different units and, as the name implies, the performance is averaged over an entire cooling season.

The SEER is the ratio of the total Btu of cooling over the cooling season divided by the watts of electrical energy input. Thus, instead of being a dimensionless number it has units of Btu/W·h. It can be converted to a dimensionless number by dividing by the conversion factor of 3.412 Btu/W·h.

A good SEER is 12 or above

See <http://www.energyideas.org/default.cfm?o=h,g,ds&c=z,z,3920> (accessed January 27, 2008) for more details on SEER measurements. The full test procedure is in the Code of Federal Regulations accessed at a DOE web site on January 27, 2008: http://www.eere.energy.gov/buildings/appliance_standards/residential/pdfs/central_ac_tp_2005.pdf



Taken from DOE web site on heat pumps (accessed January 27, 2008):
http://www.eere.energy.gov/consumer/your_home/space_heating_cooling/index.cfm/mytopic=12620

By appropriate changes in plumbing heat pumps can be used to either cool or heat the house. This chart shows the operation of the heat pump in the heating mode. Here the evaporator (where the refrigerant evaporates to extract heat from the colder outdoors) is located outside the house. The condenser (where the refrigerant condenses rejecting heat to warm the interior) is located inside the house.

The measure of performance for heating is called the heating season performance factor (HSPF). This is defined in a similar manner to the SEER for cooling; it is the ratio of the seasonal heating output in Btu divided by the seasonal power consumption in watts.

The HSPF for the most efficient heat pumps is between 8 and 10.

The SEER and HSPF ratings are used for heat pumps and air conditioners that exchange heat with the atmosphere. Geothermal heat pumps are available where heat is transferred to the nearly constant ground temperatures. The performance of such devices is measured by the usual simpler measures of coefficient of performance (COP) and energy efficiency ratio (EER).

Maximum Work

- Maximum work is done in a reversible process
- For reversible adiabatic ($Q = 0$) process, $\Delta S = 0$, $W_{\max} = \Delta U$
- Can look at other combinations of properties that interact with surroundings to remain constant
- For constant T and P , $W_{\max} = \Delta G$
 – Gibbs function, $G = H - TS = U + PV - TS$

The concept of maximum work in a reversible process is a basic result of the second law. The usual case considered in introductory thermodynamics courses is the reversible adiabatic or isentropic (constant entropy) process. If a system is at constant entropy and volume delivers work to an external source, the maximum work that can be delivered is the change in internal energy, U .

To look at maximum work for other processes, theoretical thermodynamics assumes that the system is able to maintain constant properties by reversible interactions with the surroundings. Thus maintaining constant pressure is done by reversible work on the surroundings. Maintaining constant temperature is done by reversible heat transfer with the surroundings. The analysis of maximum work for other constant property situations accounts for these interactions, but does not consider them part of the work that a system can deliver to an external object.

Perhaps the most useful result of this analysis is that the maximum work that can be delivered to an external object at constant temperature and pressure is the change in Gibbs function, ΔG . The Gibbs function is defined as $G = H - TS$. Since the enthalpy is defined as $H = U + PV$, the Gibbs function can also be defined as $U + PV - TS$.

This equation is important for fuel cells which operate at (approximately) constant temperature and pressure and convert chemical energy directly into electrical energy (work) without the intermediate step of heat production which invokes the efficiency limitations of the second law.