Introduction to Engineering Thermodynamics

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Contents

1 Energy

Lecture 1

2026-01-06

Solving problems

- List knowns and unknowns
- Draw a diagram
- State the eqn
- Show manipulation + plug in numbers (with units!)

- State final number, boxed, with units and sig digs (2, maybe 3 max)

Definition 1. The 'zeroth' law of thermodynamics is that two bodies in thermal equilibrium with a third body are also in thermal equilibrium with each other. This implies bodies are in thermal equilibrium provided they are at the same temperature, regardless of whether they are in contact.

Definition 2. First law of thermodynamics is conservation of energy: energy cannot be created or destroyed – it can only change form.

Definition 3. Second law of thermodynamics: spontaneous energy flow has a preferred direction.

A system is a region that we are studying, and the surroundings are anything outside our system. A closed system has a fixed amount of mass, so no mass can cross the boundary in/out of the system. An open system has a fixed amount of volume, but may involve mass flow in/out of the system. Energy can move in/out of an open or a closed system.

The boundary separates a system from its surroundings. It could be fixed or mobile.

Definition 4. A property is a characteristic of a system's state, and is independent of path taken to that state.

Properties can be *intensive*: independent of a system's mass, like temperature, pressure, or density.

Note. A note on temperature:

- $T(F) = 1.8T(C) + 32$
- Using the Rankine scale, $T(R) = 1.8T(K)$

This results in different numbers measuring the *ice point* and steam point, and most importantly, the *triple point* (temperature $273.16K$) △

Note. A note on pressure, the force of a fluid per unit area:

- $1Pa = 1\frac{N}{m^2}$
- $1bar = 10^5Pa$
- $1atm = 101325Pa = 1.01325bar$
- $1\frac{kgf}{cm^2} = 9.807 \cdot 10^4Pa = 0.9807bar$
- $1psi = 1\frac{lb}{in^2}$

△

Pressure

The absolute pressure is the actual pressure with respect to vacuum, or zero pressure, indicated by P. The *gauge pressure* is the difference between local atmospheric pressure and absolute pressure at a point, which is typically displayed by a measurement device. Vacuum pressures are below atmospheric pressures.

For a fluid in a container, the pressure will vary with depth. For an incompressible fluid:

$$P_{abs} = P_{atm} + \rho g h, \qquad P_{gage} = \rho g h.$$

For a fluid with variable density:

$$\Delta P = P_2 - P_1 = -\int_{h_1}^{h_2} \rho g \, dz.$$

Note that regardless of the container shape, under *hydrostatic* (still) conditions, the pressure is the same at a fixed depth within a given container containing a single fluid.

This implies Pascal's law $P_1 = P_2 = \frac{F_1}{A_1} = \frac{F_2}{A_2}$ for a hydraulic system, which is the basis of a hydraulic lift with *mechanical advantage* $\frac{A_2}{A_1}$

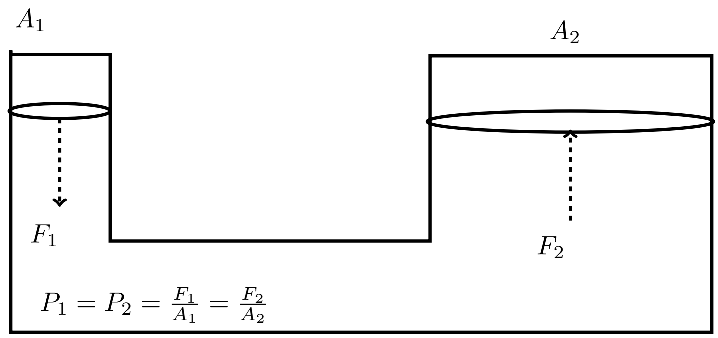

Figure 1: The mechanical advantage of a hydraulic lift

We measure absolute pressure with a barometer, so atmospheric pressure is equivalent to *barometric pressure*. This uses an inverted tube of mercury with a pocket of air. A manometer is a tube measuring the difference in pressure between two points in a closed system, therefore displaying gauge pressure.

Specific properties are intensive properties defined as extensive properties per unit mass $e = \frac{E}{m}, \quad c = \frac{C}{m}$, typically denoted by a lower case letter. Notable ones include:

- Specific volume is volume per unit mass

$$\nu \left(\frac{m^3}{kg}\right) = \frac{V}{m} = \frac{1}{\rho}.$$

- Specific gravity is the ratio of a substance's density to the density of a standard substance at a fixed temperature, e.g. against water at $4°C$

$$SG\,(\text{ratio}) = \frac{\rho_i}{\rho_{H_2O}}.$$

Properties can be *extensive*: depend on the extent of the system, like mass or volume.

1.1 Forms of Energy

Thermodynamics deals with the change in total energy, $E = U + KE + PE$.

Definition 5. Macroscopic forms of energy are system-level energy with respect to some reference frame.

Kinetic energy KE is the macroscopic energy of motion with respect to a reference frame. Potential energy PE is the macroscopic potential energy (gravitational) within a field.

Definition 6. Microscopic forms of energy are related to the microstructure and molecular activity.

Internal energy U is the sum of all microscopic forms of energy.

2026-01-08

Lecture 2

Definition 7. A simple compressible system involves no electrical, magnetic, gravitational, motion, or surface tension effects.

The state postulate gives that for simple compressible systems, only two independent, *intensive* properties define the system. This could be temperature and specific volume or temperature and pressure (not including phase changes, where $T_{\text{phase change}} \implies P_{\text{phase change}}$).

1.2 Processes and Paths

Thermodynamics studies *equilibrium* states:

- Thermal: uniform temperature throughout the system
- Mechanical: uniform pressure throughout the system
- Phase: the mass of each phase stays constant
- Chemical: chemical composition is constant, i.e. no chemical reactions occur

Changing from one equilibrium to another undergoes a *process*, in which it transforms through a series of states, or a *path*. Processes are defined by the path, including the initial and final states, as well as what is our system vs. surroundings.

We can visualize processes by plotting thermodynamic quantities against each other, like pressure, temperature, volume/specific volume, etcetera.

- Isothermal process: temperature remains constant;
- Isobaric process: pressure remains constant;

- Isochoric/isometric process: *specific* volume remains constant;
- Cycle: initial and final states are identical.

Processes that remain infinitesimally close to an equilibrium state along their whole path are called *quasi static* or *quasi equilibrium* processes.

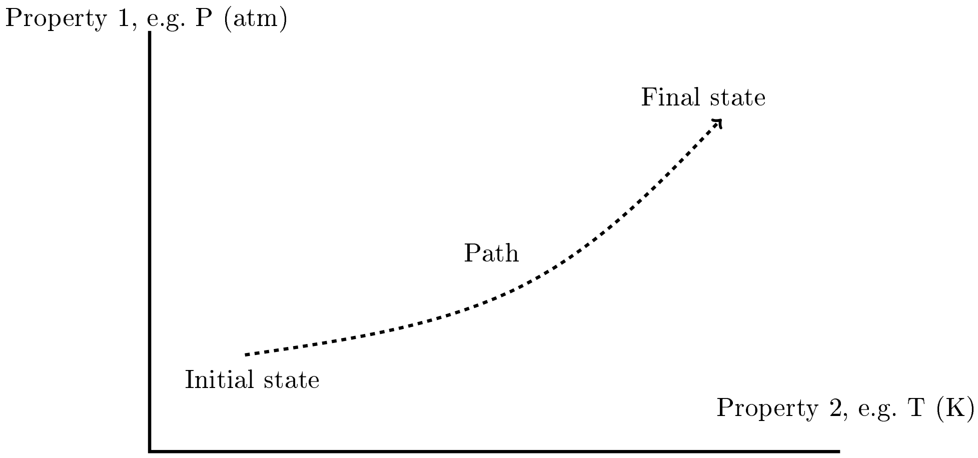

Figure 2: Example of a path and process

Lecture 3 2026-01-13

2 Heat and Work

> **Definition 8.** Heat is the form of energy transferred through a temperature difference. Heat, Q, transfer can be expressed in terms of the rate of heat transfer as:
>
> $$Q = \int_{t_1}^{t_2} \dot{Q}\, dt.$$
>
> And can be expressed per unit mass as:
>
> $$q = \frac{Q}{m}.$$

During an adiabatic process, no heat is exchanged with the surroundings, either by virtue of a fast process or good insulation.

Definition 9. Work is the energy transferred through a force acting over a parallel distance. We can express total work as:

$$W = \int_{t_1}^{t_2} \dot{W}\, dt.$$

And per unit mass as:

$$w = \frac{W}{m}.$$

Electrical power, $\dot{W} = VI$, can be integrated to find electrical work, $W = \int_{t_1}^{t_2} VI\, dt$. Mechanical power, $\dot{W} = \boldsymbol{F} \cdot \boldsymbol{v}$, is only non-zero for a force acting on the boundary of a system which moves parallel to the force. Mechanical power can be integrated to find $W = \int_{t_1}^{t_2} \boldsymbol{F} \cdot \boldsymbol{v}\, dt = \int_{s_1}^{s_2} \boldsymbol{F} \cdot d\boldsymbol{s}$.

Forms of mechanical work:

- Shaft work:

  A force through a moment arm r generates a torque through n rotations $s = 2\pi rn$.

  $$T = \boldsymbol{r} \times \boldsymbol{F}.$$

  This results in work and power:

  $$W_{sh} = 2\pi nT \implies \dot{W}_{sh} = 2\pi \dot{n} T.$$

- Spring work:

  A force changing the displacement of a spring from equilibrium of $x_1 \to x_2$:

  $$W = \Delta E = \int F_s\, dx = \frac{1}{2} k \left(x_2^2 - x_1^2 \right).$$

- Work done on elastic solid bars:

  Solid bars behave as springs under the influence of a force.

  $$W_{elastic} = \int F\, dx = \int_{x_1}^{x_2} \sigma_n A\, dx.$$

  Where A is the area and σ_n is the stress.

- Stretching a liquid film:

  $$W_{surface} = \int_{A_1}^{A_2} \sigma_s\, dA, \quad dA = 2bdx, \quad F = 2b\sigma_s.$$

Sign convention: We define heat transfer *into* a system, and work *done by* a system, as positive (heating a cup of coffee + its eventual expansion due to steam both are positive heat/work transfer). when heat flows out of a system, or work is done on that system, we define the change in energy as negative.

Note. Both heat and energy are *boundary* phenomena, as their method of transfer occurs on the boundaries (cross-boundary). Both are associated with a process (change in energy), not a state. Note that both heat and work are path-dependent, i.e. they are not point functions, or properties of the system. △

3 Properties of Pure Substances

Definition 10. A pure substance has fixed chemical composition throughout. We consider air to be pure even though it is a mixture.

Phase changes of pure substances:

- A compressed or subcooled liquid is not about to vaporize;
- A saturated liquid is about to vaporize;
- A saturated liquid-vapour mixture have both phases coexisting;
- Saturated vapour is a vapour that is about to condense;
- Superheated vapour is vapour that is not about to condense, i.e. not saturated.

The saturation temperature T_{sat} is the temperature at which a pure substance changes phase at a given *pressure*. The saturation pressure P_{sat} is the pressure at which a pure substance changes phase at a given *temperature*. We can find this in a steam table for water.

Latent heat is the amount of energy absorbed or released during a phase change process – constant regardless of phase change direction! Note that the magnitude of latent heat of vaporization is dependent on the pressure/temperature the phase change occurs at. Also known as the *enthalpy of vaporization*, this is the amount of energy per unit mass of saturated liquid required to vaporize the liquid under the given conditions.

A property diagram illustrates information similar to a steam table, analysing T-v, P-v, or P-T phase change points for pure substances. Note that we often use specific volume, as the intrinsic property allows us to see the relationship other changes have with volume. The critical point is the point at which the saturated liquid and vapour states are identical. At this point, the latent heat of vaporization is 0. Under the curve, we have a liquid + vapour mixture. Left of the curve is subcooled liquid, right of the curve is superheated vapour.

Lecture 4

2026-01-15

We can define the *quality* x to be the ratio of vapour mass to total mass of the mixture (ONLY for mixtures of saturated phases). Points sitting on the curve are under saturated conditions for a given pressure. Left of the critical point, it is a saturated liquid with quality 0. Right of the critical point, it is a saturated vapour with quality 1. For a horizontal line $T = T@saturation$ connecting two points (at a given pressure), the quality transitions from 0 to 1.

Given the specific volume of a saturated mixture, we can use a tie line to find the fractions of saturated liquid and vapour.

$$x = \frac{v_{avg} - v_f}{v_{fg}}.$$

Where v_f is the specific volume of the saturated liquid, v_g of the saturated gas, and v_{avg} is the intermediate, or mixture specific volume.

$$v_{avg} = v_f + xv_g.$$

By cyclic permutation, we can use the same formula for the intermediate (specific) internal energy $u_{avg}(\frac{kJ}{kg})$, enthalpy $h_{avg}(\frac{kJ}{kg})$, and entropy $s_{avg}(\frac{kJ}{kg \cdot K})$. Enthalpy $H\ (J)$ is a new extensive property that describes the Q_{in} and Q_{out}, where h is the specific enthalpy.

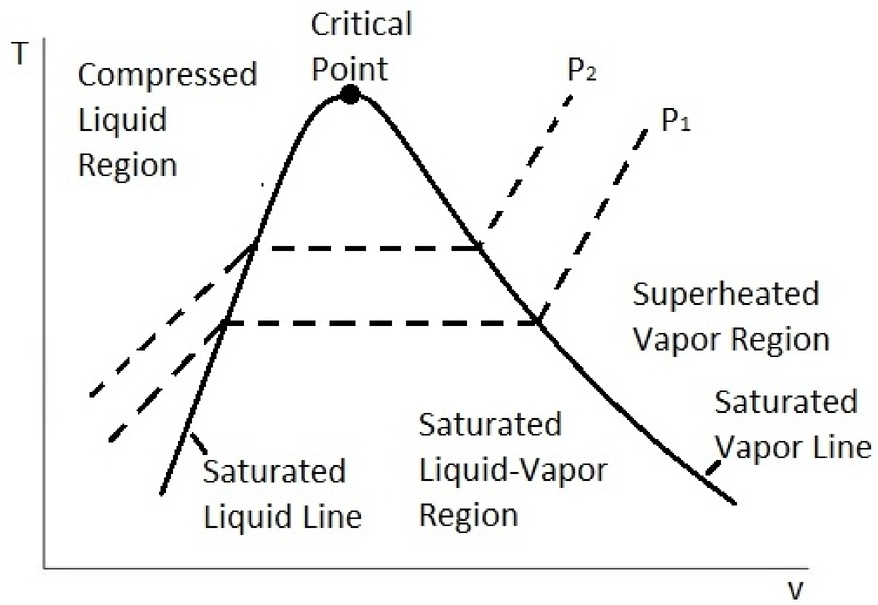

Figure 3: A property diagram showing the liquid and gas saturation lines. The peak of the curve is the critical point. Note that with both the temperature and v, the pressure can be calculated (see state postulate).

2026-01-20 **Lecture 5**

Compressed Liquids

When extrapolating properties for compressed liquids, we note:

- Properties depend stronger on temperature than on pressure, so the specific volume, internal energy, or enthalpy are all well approximated by their values at saturated liquid:

$$u \approx u_{f@T}.$$

- For enthalpy, we can refine the formula to include pump work as:

$$h \approx h_{f@T} + \nu_{f@T} \left(P - P_{sat@T}\right).$$

3.1 Equations of State

Definition 11. An equation of state relates the pressure, temperature, and specific volume of a substance. The ideal gas equation of state is an accurate equation of state (sufficiently high T and low P):

$$P\nu = RT.$$

Where $R = \frac{R_u}{M}$ is the gas constant, M is the molar mass in $\frac{kg}{kmol}$, and the ideal gas constant is $R_u = 8.31447 \frac{kJ}{kmol \cdot K}$ or equivalent.

Definition 12. The compressibility factor Z is a factor that accounts for the deviation from ideal gas behaviour:

$$Z = \frac{P\nu}{RT} = \frac{\nu_{actual}}{\nu_{ideal}}.$$

Where $\nu_{ideal} = \frac{RT}{P}$. $Z = 1$ for ideal gases, and $Z < 1$ or $Z > 1$ for real gases.

Z is about the same at the same T_r and P_r, where $P_r = \frac{P}{P_{cr}}$ and $T_r = \frac{T}{T_{cr}}$ are the reduced pressure and temperature, respectively. $\nu_R = \frac{\nu_{actual} P_{cr}}{RT_{cr}}$ is the pseudo-reduced specific volume. Note that T_{cr} and P_{cr} are the critical temperature and pressure.

Lecture 6

2026-01-22

Definition 13. Moving boundary work is the work done by expansion and compression of a piston device.

$$\sigma W_b = Fds = PAds = PdV \implies W_b = \int_{V_1}^{V_2} p\, dV.$$

We define positive boundary work for expansion, as it is work done by the system.

Note that we are assuming a closed system (mass constant) and a quasi-equilibrium process.

Moving boundary work is the area under a $P - V$ curve, meaning that boundary work is a path-dependent value.

- Under constant pressure (isobaric), our formula collapses to:

  $$W_b = P_0 (V_2 - V_1) = mP_0 (\nu_2 - \nu_1).$$

  Corresponding with a rectangle on a $P - V$ graph.

- Under constant volume (isochoric), no work is done, as this is a vertical line on a $P - V$ graph.

- Under constant temperature (isothermal), our formula collapses using ideal gas law to:

  $$W_b = P_1 V_1 \ln\left(\frac{V_2}{V_1}\right).$$

- For a *polytropic process*, where $PV^n = \text{const}$, we can find the work done as:

  $$W_b = \frac{mR(T_2 - T_1)}{1 - n}.$$

  Assuming an ideal gas.

- For a system expanding against a linear spring, meaning a straight line on a $P - \nu$ graph:

  $$W_b = P_0 \Delta V + \frac{1}{2}\Delta P \Delta V.$$

  Re derive this by integrating force over distance.

2026-01-27 **Lecture 7**

4 Energy Analysis

4.1 Closed Systems

When a closed system's energy changes during of process, we can quantify the change in energy as:

$$\Delta E = \Delta U + \Delta KE + \Delta PE = Q_{net,in} + W_{net,in} = Q_{in} - Q_{out} + W_{in} - W_{out}.$$

This equation uses pure magnitudes, but we can used signed quantities as:

$$Q_{in} - W_{out} = \Delta E.$$

Since heat in and work out are both defined as positive, but have opposite effects on the total energy of the system (hence the negative sign). Note that for stationary systems, $\Delta E = \Delta U_0$.

Definition 14. Specific heat is the heat required to increase the temperature of a substance. Specific heat at constant volume c_v is normalized to unity mass of a substance by one degree, under isochoric conditions. Specific heat at constant pressure c_p is normalized to unity mass of a substance by one degree under isobaric conditions.

Using specific heat, a fixed mass in a stationary, isochoric process undergoes a change in specific energy as:

$$\delta e = \delta q - (\delta w = 0) = c_v dT \implies c_v = \frac{\partial u}{\partial T}.$$

For an isobaric process, the internal energy changes as:

$$\delta e = \delta q - \delta w = c_p dT - P dv = du.$$

Rearranging to solve for the differential change in specific enthalpy:

$$c_p dT = du + P dv = dh \implies c_P = \frac{\partial h}{\partial T}_{Pconst}.$$

This shows how c_v relates to changes in internal energy, while c_p relates to changes in enthalpy. They are the rate of change of each associated quantity with respect to temperature. For an ideal gas:

$$h = u + Pv = u + RT.$$

Where for ideal gases, u, h, c_p, and c_v vary with temperature only, and obey:

$$\Delta u = \int c_v(T)\, dT$$
$$\Delta h = \int c_p(T)\, dT.$$

The base values of c_{p_0} and c_{v_0}, or zero-pressure specific heats are the ideal gas behaviour versions, and are approximated as constant with temperature for ideal gases. Alternatively, we could use an average value for c_p and c_v.

Note that while these integrals may be good approximations of u and h if our ideal assumptions are met, calculating via tables or using the polynomial formulas for c. For enthalpies of compressed liquids, we can use:

$$h_{@p,t} = h_{f@t} + \nu_{f@t}\left(P - P_{sat@T}\right).$$

Note. These properties are state-dependent, but are not differentiated for solids and liquids due to negligible dV under dT. c_p is always greater than c_v under given conditions, since the c_p process 'loses' energy to boundary work, requiring more energy to increase the temperature (du). △

Since $dh = du + RdT \implies dh = c_p dT = (c_v + R)\, dT$, then $c_p = c_v + R\left(\frac{kJ}{kg\cdot K}\right)$, or on a molar basis, $\bar{c}_p = \bar{c}_v + R_u$.

Lecture 8

2026-01-29

4.2 Steady Flow Systems

Mass is constant in a closed system, but in control volumes this is not the case. The mass flow rate $\dot{m}\left(\frac{kg}{s}\right)$:

$$\dot{m} = \rho v_{avg} A_c = \rho \dot{V}.$$

Describes the amount of mass moving through a system per unit time, using an average speed to describe non-uniform speed. We use this to describe the mass balance of the system:

$$\dot{m}_{in} - \dot{m}_{out} = \frac{dm_{cv}}{dt} \implies m_{in} - m_{out} = \Delta m_{cv}.$$

A steady-flow process has $\frac{dm_{cv}}{dt} = 0$, meaning that the mass flow rates in and out of the system are equal.

Definition 15. Flow work, or flow energy is the energy required to move mass in or out of the control volume to maintain continuous flow:

$$F = PA \implies W_{flow} = FL = PAL = PV, \quad w_{flow} = P\nu.$$

Lecture 9

2026-02-03

Recall that for a closed system, when considering work, we assumed that the kinetic energy and potential energy were unchanging, i.e. the energy of a system was contained in U. In an open system we must account for these types of energy:

$$\begin{aligned} e &= u + ke + pe = u + \frac{v^2}{2} + gz \\ h &= u + P\nu \\ \theta &= P\nu + e = h + ke + pe. \end{aligned}$$

Observe that the enthalpy 'captures' the flow energy by default. We can obtain final energy balance relations for an open system:

$$Q - W = \Delta H + \Delta KE + \Delta PE.$$

Here are some examples of static or steady flow devices, which follow mass balance:

- Turbine

  Convert thermal or flow energy to work inside a control volume, or static flow system. It generates w from flow work h. The change in ke and pe is negligible.

- Compressor

  Convert w_{in} into h (increase the pressure) at relatively constant ke and pe:

  $$\dot{W}_{in} + \dot{m}h_1 = \dot{Q}_{out} + \dot{m}h_2.$$

  Accounting for the rate of heat loss $\dot{Q}_{out}$. This increases the pressure of a vapour stream

- Pump

  Convert w_{in} into h. This increases the pressure of a liquid stream.

- Throttling valve

  Flow restricting single stream device that lowers the pressure of the fluid, sometimes accompanied by drop in temperature. The $q = w = \Delta ke = \Delta pe = 0$, meaning the energy balance is contained in h:

  $$u_1 + P_1\nu_1 = u_2 + P_2\nu_2.$$

  Internal and flow energies are interchanged.

- Mixer

  Combine different $\dot{m}_i h_i$ from different sources.

- Heat Exchanger

  The net $\dot{Q}$ and $\dot{W}$ is about 0, but inlet $\dot{m}_i h_i$ are transformed into different $\dot{m}_e h_e$.

- Nozzle and Diffuser

  Nozzles increase the kinetic energy at the expense of pressure, and vice versa for a diffuser. Convert between $\Delta\dot{KE} = \frac{\dot{m}}{2}\left(v_e^2 - v_i^2\right)$ and flow energy in h

  $$\dot{E}_{in} = \dot{E}_{out} \implies \dot{m}\left(h_1 + \frac{vel_1^2}{2}\right) = \dot{m}\left(h_2 + \frac{vel_2^2}{2}\right).$$

  Sometimes we must take into account Δpe.

2026-02-05 **Lecture 10**

4.3 Transient Flow Systems

Definition 16. An unsteady-flow process, or transient-flow precess, involve changes within the control volume with time.

$$\Delta m_{system} = m_{final} - m_{initial} = m_{in} - m_{out}.$$

Most transient-flow processes are well represented by uniform-flow processes, where we assume inlet and exit flow is approximately steady. We treat the fluid properties over the cross-section of the input and output as constant, or averaged to a constant.

While the mass balance equations are simple, our energy balance looks different than in previous systems:

- Closed system: $Q - W = \Delta U$

- Static flow: $\dot{E}_{in} = \dot{E}_{out}$, $Q - W = \Delta H$ (ignoring kinetic and potential energy but accounting for flow energy)
- Transient-flow: $E_{in} - E_{out} = \Delta E_{system}$

To quantify our changing total energy:

$$Q_{in} - W_{out} = (m_2 u_2 - m_1 u_1) + (m_e h_e - m_i h_i) .$$

We modify our equation for the closed system work to account for the net flow energy in and out of the system.

Lecture 11 2026-02-10

5 Second Law

The second law of thermodynamics dictates that processes may occur in one direction, but not the reverse. All work can be converted to heat, but converting heat to work with a heat engine is never 100% efficient. This implies that processes will have a direction and a quality, describing the degree of degradation or completion involved. Processes must satisfy conservation of mass, the first law of thermodynamics, and the second law of thermodynamics.

A *thermal energy reservoir* or heat reservoir is a body with a large thermal energy capacity that can absorb or supply (sink or source) finite amounts of heat without a change in temperature.

Heat engines are devices that convert heat to work.

- Q_{in} is heat supplied to steam in the boiler from a high temperature source;
- Equivalently, Q_H is the magnitude of heat transfer between the high-temperature medium at T_H and the cyclic device;
- Q_{out} is heat lost without doing useful work to a low-temperature sink;
- Equivalently Q_L is the magnitude of heat transfer between the low-temperature medium at T_L and the cyclic device;
- W_{out} is useful work delivered by expanding steam in turbine;
- W_{in} is work required to compress water to boiler pressure.

The total work out from a heat engine is:

$$W_{net,out} = W_{out} - W_{in} = Q_{in} - Q_{out} = Q_H - Q_L.$$

The total thermal efficiency is the amount if input heat converted to work:

$$\eta_{th} = \frac{W_{net,out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}.$$

Note that some heat rejection in a condenser is required to complete the thermodynamic cycle.

Definition 17. The Kelvin-Planck statement states that it is impossible for any cyclic device to receive heat from a single reservoir and produce net work. Therefore, no heat engine can be 100% efficient, and in fact, most power plants are about 40%.

Transferring heat from low to high temperatures requires a refrigerator device, which typically uses a vapour-compression refrigeration cycle with a refrigerant fluid.

Low pressure liquid enters an evaporator and absorbs heat from the low-temperature reservoir to evaporate. It is then compressed into a high pressure vapour, requiring W_{in}, at which point it enters a condenser and releases heat to a high-temperature reservoir. The high pressure liquid is passed through a throttle valve so it is a low pressure liquid/vapour again.

2026-02-12 **Lecture 12**

Efficiency of a refrigerator can be described via the coefficient of performance:

$$COP_R = \frac{Q_L}{W_{net,in}} = \frac{1}{Q_H/Q_L - 1}.$$

Where $W_{net,in} = Q_H - Q_L$. For a heat pump, this is:

$$COP_{HP} = \frac{Q_H}{W_{net,in}} = \frac{1}{1 - Q_L/Q_H}.$$

This metric describes the desired energy transfer divided by the required work input. For example, in a refrigerator, we desire the transfer of heat away from our cold reservoir, Q_L. Note that $COP_R \approx 1.8$, $COP_{HP} \approx 2 - 3$, and $COP_{HP} = COP_R + 1$

Note. For reversible cycles, we can use absolute temperatures T_H and T_L (Kelvin) to replace our Q_H and Q_L:

$$\eta_{th} = 1 - \frac{Q_L}{Q_H}(\text{any heat engine}), \quad \eta_{\text{th,rev}} = 1 - \frac{T_L}{T_H}.$$

Where $\eta_{\text{th,rev}}$ is the maximum possible efficiency between a given temperature differential, represented by a Carnot heat engine. Therefore, for a Carnot refrigerator or heat pump:

$$COP_{R,rev} = \frac{1}{T_H/T_L - 1}, \quad COP_{HP,rev} = \frac{1}{1 - T_L/T_H}.$$

Which bound the theoretical max COP. △

Definition 18. The Clausius statement is that it is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from low to high temperatures. There must be some consumption of energy in the form of work. This is a statement of the second law of thermodynamics.

Both the Kelvin-Planck and Clausius statements are equivalent. A 100% efficient heat engine would allow for a refrigerator to transfer Q_L from low to high temperatures without input work, showing how if one statement is violated, the other is as well.

A perpetual-motion machine (PMM) violates the laws of thermodynamics.

- A PMM1 generates free energy;
- A PMM2 is 100% efficient.

A *reversible* process can be reversed without leaving a trace on the surroundings. Irreversibilities, such as friction, unrestrained expansion, mixing of two fluids, heat transfer across a finite temperature difference, electric resistance, chemical reactions, and inelastic deformation of solids, render processes irreversible. Typically, efficiency of reversible processes is better than that of irreversible processes:

$$\eta_{th,real} \leq \eta_{th,rev}.$$

Recall that for a heat engine, thermal efficiency is defined as:

$$\eta_{th} = \frac{W_{\text{out}}}{Q_{\text{in}}} = \frac{Q_H - Q_L}{Q_H} = 1 - Q_L/Q_H.$$

Which can be replaced by absolute temperatures given a reversible, or Carnot, heat engine. This ideal efficiency bounds the efficiency of a real device.

A process is *internally* reversible if there are no irreversibilities within the boundaries. A process is *externally* reversible if there are no irreversibilities outside the system boundaries. A system that is both internally and externally reversible is *totally reversible*.

Lecture 13

2026-02-24

5.1 Entropy

Recall that a property is a path-independent quantity (state function), meaning its differential is exact, and its cyclic integral is 0.

Definition 19. Entropy is an extensive property of a system, defined through a reversible process, describing the molecular kinetics (disorder) of the system:

$$dS = \left(\frac{\delta Q}{T}\right)_{rev} \quad \left(\frac{kJ}{K}\right).$$

It is strictly related to heat, not work, and this exact differential only holds for a reversible process.

For reversible process:

$$\Delta S = \int \frac{\delta Q_{rev}}{T} \implies \oint \left(\frac{\delta Q}{T}\right)_{int,rev} = 0.$$

In general:

$$\oint dS = 0.$$

A thermal energy reservoir has an assumed constant temperature, so the change in entropy is $\Delta S_{res} = \frac{Q_{res}}{T_0}$.

Theorem 1. The Clausius inequality states that:

$$\oint \frac{\delta Q}{T} \leq 0.$$

The equality $\oint \frac{dQ}{T} = 0$ will hold for totally or an internally reversible processes, which implies the efficient processing. Any irreversible process will strictly satisfy the inequality < 0.

More generally, for a process:

$$\Delta S = \int_1^2 \frac{\delta Q}{T} + S_{gen} \geq \int_1^2 \frac{\delta Q}{T}.$$

Note that $S_{gen} = 0$ only for a reversible process, meaning equality only holds in this case. Otherwise, $S_{gen} > 0$.

Entropy characterises the second law, in that processes occur in a certain direction only (that which increases entropy). Entropy is not generally conserved outside of idealized reversible processes, since entropy generation is a measure of the irreversibilities of the system.

Finding entropy from tables follows our typical properties: interpolation via the quality x, and assuming s of a compressed liquid is that of the saturated liquid at the same temperature:

$$s_{comp.liq.@T} \approx s_{f@T} \left(\frac{kJ}{kg \cdot K}\right), \quad \Delta S = m\Delta s.$$

We can define a entropy pseudo-balance for *closed systems*:

$$S_2 - S_1 = \frac{Q_{in,sys}}{T_{sys}} + S_{gen,internal}.$$

Where $S_{gen,internal} = 0$ for reversible processes, and $Q_{in,surr} = 0$ for adiabatic systems. A system that is adiabatic and reversible is labelled *isentropic*, which must have $S_2 - S_1 = 0$.

When considering the change in total entropy of our system and surroundings, it must always be greater than or equal to 0:

$$\Delta S_{\text{gen,total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0.$$

This restricts the direction of any given process: a process can never act to decrease the total entropy.

For an internally reversible process, where our definition of entropy holds, we have:

$$q_{\text{int,rev}} = \int_1^2 T\, ds.$$

This implies that on a $T - s$ diagram, for an internally reversible process, the area under the curve is equal to the net heat transfer.

$$\sum \frac{Q_{in}}{T_{surr}} + \sum m_i s_i - \sum m_e s_e + S_{gen} = 0.$$

As we take into account heat-transferred entropy. For unsteady-flow:

$$\sum \frac{Q_{in}}{T_{surr}} + \sum m_i s_i - \sum m_e s_e + S_{gen} = m_2 s_2 - m_1 s_1.$$

This accounts for both heat-transferred and mass-transferred entropy.

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The Boltzmann relation quantifies entropy as:

$$S = k_B \ln \Omega.$$

Where $k_B = 1.3806 \cdot 10^{-23} \frac{J}{K}$ is the Boltzmann constant, and Ω is the total number of possible micro states of the system.

> **Definition 20.** The third law of thermodynamics states that the entropy of a pure crystalline substance at absolute zero is $S = 0$, since no molecule has uncertainty. Entropy relative to this point is *absolute entropy*.

We have some differential entropy change relations:

- $\delta Q_{int,rev} = \delta W_{int,rev,out} = dU$
- $\delta Q_{int,rev} = Tds$
- $\delta W_{int,rev,out} = PdV$
- $TdS = dU + PdV$
- $Tds = dh - \nu dp$

For liquids and solids, their incompressibility yields:

$$s_2 - s_1 = \int_1^2 c_v \frac{dT}{T} \approx c_{avg} \ln \frac{T_2}{T_1}.$$

For an ideal gas:

$$s_2 - s_1 = \int_1^2 c_p \frac{dT}{T} - R \ln \frac{P_2}{P_1} \approx c_{p,avg} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}.$$

$$s_2 - s_1 = \int_1^2 c_v \frac{dT}{T} + R \ln \frac{\nu_2}{\nu_1} \approx c_{v,avg} \ln \frac{T_2}{T_1} + R \ln \frac{\nu_2}{\nu_1}.$$

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2026-03-03

Note that s_i^0 is the entropy of an ideal gas with respect to absolute zero, found as $s^0 = \int_0^T c_p (T) \frac{dT}{T}$. It represents only the temperature dependent part of entropy.

Recall that isentropic processing implies entropy is conserved, so our two Tds equations for an *ideal gas* become:

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{\nu_1}{\nu_2}\right)^{\frac{R}{c_v}}$$

$$\left(\frac{P_2}{P_1}\right) = \left(\frac{\nu_1}{\nu_2}\right)^{\frac{c_p}{c_v}}.$$

It's important to remember that these relations hold for ideal gases. For real gases, we can use the entropy departure factor Z_S to link the ideal enthalpy change $S_2^* - S_1^*$ to the real enthalpy changes $S_2 - S_1$.

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6 Entropy Analysis

In a reversible process, we can define:

$$\delta q_{rev} = Tds = dh - \nu dP \implies Tds = dh - \nu dP.$$

Subbing into our canonical steady-flow equation, we can alternatively obtain:

$$dw_{in} = \nu dP + dke + dpe.$$

Let's imagine a steady flow system involving no work interactions. We can integrate the previous equation to recover the Bernoulli equation:

$$\nu (P_2 - P_1) + \frac{v_2^2 - v_1^2}{2} + g (z_2 - z_1) = 0.$$

Definition 21. Isentropic efficiency, or adiabatic efficiency measures the deviation of an actual process from the idealized, most efficient one.

$$\eta = \frac{w_{a,out}}{w_{s,out}}.$$

For example, an isentropic adiabatic turbine forms a vertically down-pointing line on a $h - s$ graph, however in a real adiabatic turbine, the entropy of the exhaust will increase slightly with respect to the inlet.

$$\eta_T = \frac{\text{actual turbine work}}{\text{isentropic turvine work}} \approx |\frac{h_1 - h_{2a}}{h_1 - h_{2s}}|.$$

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Another example is the isentropic efficiency of a pump:

$$\eta_p = \frac{w_{in,s}}{w_{in,a}} \approx \frac{\nu (P_2 - P_1)}{h_{2a} - h_1}.$$

Where the isentropic, or ideal, work in is always smaller than the actual work in. Our simplification assumes kinetic and potential energies are negligible.

For the best performance of a compressor, we similarly take the ratio of isentropic work in to actual work in:

$$\eta_c = \frac{w_s}{w_a} \approx \frac{h_{2s} - h_1}{h_{2a} - h_1}.$$

Where we simplify assuming kinetic and potential energies are negligible.

For a nozzle, we take the isentropic efficiency to by the ratio of exit kinetic energies:

$$\eta_n = \frac{V_{2a}^2}{V_{2s}^2}.$$

6.1 Entropy Balance

Definition 22. The entropy change of a system is equal to the net entropy transfer across the system boundary and the entropy generated by the process.

$$S_{in} - S_{out} + S_{gen} = \Delta S_{sys}.$$

Entropy can be transferred across a boundary through heat flow:

$$S_{\text{heat}} = \int_1^2 \frac{\delta Q}{T_{\text{boundary}}} = \frac{\Delta Q}{T_{\text{const}}}.$$

Entropy can be transferred by mass flow (in steady or transient flow systems):

$$S_{\text{mass}} = ms.$$

Entropy can be generated during a process via S_{gen}.

$$S_{\text{gen}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}, \quad \Delta S_{\text{surr}} = \frac{\Delta Q}{T}.$$

For a closed system, our net equation looks like:

$$\sum \frac{Q_{\text{in,sys}}}{T} + S_{\text{gen}} = m\left(s_2 - s_1\right), \quad Q_{\text{in,sys}} = -Q_{\text{in,surr}}.$$

For a control volume, we must take into account the mass moving through the inlet and exit:

$$\sum \frac{Q_{\text{in,sys}}}{T} + \sum m_i s_i - \sum m_e s_e + S_{\text{gen}} = S_2 - S_1.$$

Note. For steady flow, $\frac{dS}{dt} = 0$, so the right hand side of the above equation is simplified as $S_2 - S_1 = 0$. For transient flow, we must take into account the change in total entropy in the CV using these terms. Also pay attention to modifiers like adiabatic, which will simplify equations by dropping heat transfer. △

Lecture 18

2026-03-17

7 Cycles

A cycle is a series of processes that starts and ends at the same state. An *ideal cycle* is made up of internally reversible processes, which resembles but idealizes a real process. While internally reversible, they are not necessarily externally reversible, meaning it doesn't generate entropy internally, but may do so at the interfaces.

Reversible cycles, such as the Carnot cycles, take this one step further by being totally reversible, and as such are not realistic. They have the highest thermal efficiency for any heat engine operating across two set temperature limits.

$$\eta_{th} = \frac{W_{\text{net}}}{Q_{\text{in}}}.$$

Assumptions we make in power cycles:

- There is no friction (e.g. fluids do not experience pressure drops in pipes);
- All expansion and compression processes are quasi-equilibrium processes (allows us to assume internally reversible, which are transitions through equilibrium states);
  - On $P - \nu$ diagrams, these are isobaric, isobaric, or isothermal lines, representing maximum-work-producing or minimum-work-consuming processes.
  - On $T - s$ diagrams, these are isothermal, isentropic, or polytropic lines.
- All pipes are well-insulated;

Note. On a $P - \nu$ (and a $T - s$ diagram for internally reversible cycles), the area enclosed by the cyclic curve is $W_{\text{net,out}}$. On a $T - s$ diagram, the ratio of the area enclosed by the cyclic curve to the area under the heat-addition process curve represents the thermal efficiency of the cycle. △

7.1 Gas Power Cycles

The *air-standard* assumptions are:

- Air circulates in a closed loop behaves as an ideal gas;
- All processes are internally reversible;
- Combustion is replaced by a heat-addition process;
- Exhaust is replaced by a heat-rejection process that restores initial states.

If we can assume constant specific heats oat $25°C$, then they further satisfy the cold-air-standard assumptions.

Reciprocating engines are described by their compression ratio:

$$r = \frac{V_{\text{max}}}{V_{\text{min}}} = \frac{V_{\text{BDC}}}{V_{\text{TDC}}}.$$

Where the minimum and maximum volumes describe the bounds on the piston motion. We can alternatively label these as TDC and BDC, for top dead centre and bottom dead centre. This is applicable to spark-ignition (Otto cycles) and compression-ignition (diesel cycle) engines.

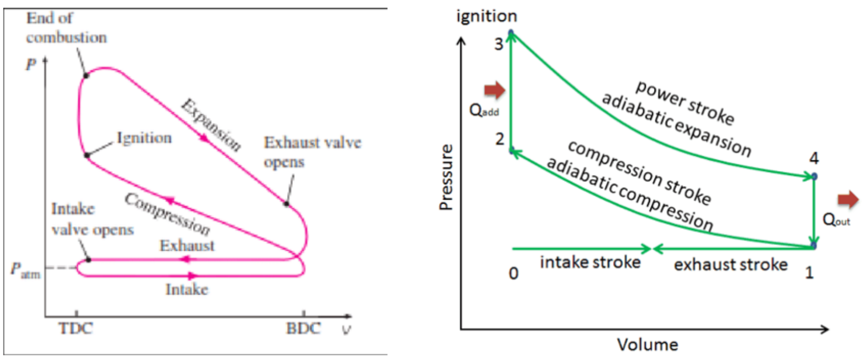
From these bounds, we can calculate a mean effective pressure, which is the constant pressure at which an expansion from V_{min} to V_{max} will generate the same amount of work as the cycle:

$$\text{MEP} = \frac{w_{out}}{\nu_{\text{max}} - \nu_{\text{min}}}.$$

Note. Note that at V_{min} for a spark-ignition engine, we do not want to exceed the auto-ignition temperature of the gas as combustion is controlled by the spark plug. However, diesel cycle engines rely on this auto-ignition. Therefore, V_{min} is smaller for compression-ignition engines, and therefore the compression ratio is higher! △

The ideal Otto cycles is given by:

1. An isentropic compression representing compression of an air-fuel mixture;
2. A constant volume heat addition followed by an isentropic expansion to represent combustion;



Actual Otto Cycle — Ideal Otto Cycle

Figure 4: A comparision of the ideal vs. real Otto cycle. Note that modelling combustion and exhaust with heat transfer cycles results in losing the exhaust and intake strokes, as we assume air is contained in a closed loop. However, when calculating power, we consider the additional strokes in our ideal cycle, even if there is no work done.

3. A constant volume heat rejection process representing an exhaust cycle.

Doing some analysis, we can first find the compression ratio as:

$$r = \frac{V_{\text{max}}}{V_{\text{min}}} = \frac{V_1}{V_2} = \frac{\nu_1}{\nu_2}.$$

The thermal efficiency is given by:

$$\eta_{\text{th,Otto}} = \frac{w_{\text{net}}}{q_{\text{in}}} = 1 - \frac{q_{\text{out}}}{q_{\text{in}}} = 1 - \frac{T_1\left(\frac{T_4}{T_1} - 1\right)}{T_2\left(\frac{T_3}{T_2} - 1\right)}.$$

We can also use our isentropic ideal gas equations to express this as:

$$\eta_{\text{th,Otto}} = 1 - \frac{1}{r^{k-1}}.$$

Lecture 19

2026-03-19

The Diesel Cycle

The ideal diesel cycle, or compression-ignition engine cycle, is:

- An isentropic compression;
- A constant-pressure heat addition;
- An isentropic expansion;
- A constant volume heat rejection.

The cutoff ratio is defined as the ratio of the volume after and before the constant pressure heat addition, from state $2 \to 3$:

$$r_c = \frac{V_3}{V_2} = \frac{\nu_3}{\nu_2}.$$

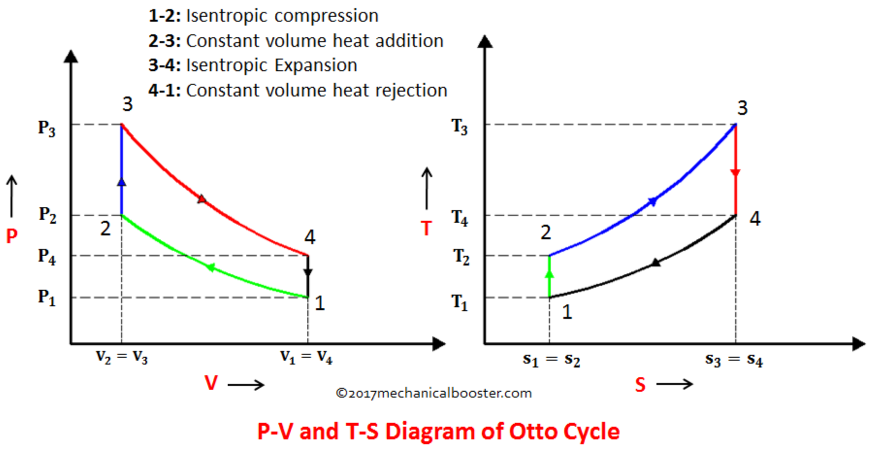


Figure 5: Property diagrams for the Otto cycle.

For the Otto cycle, this would be 1.

The thermal efficiency is given by:

$$\eta_{\text{th,Diesel}} = \frac{w_{net,out}}{q_{in}} = 1 - \frac{T_4 - T_1}{k\,(T_3 - T_2)} = 1 - \frac{1}{r^{k-1}}.$$

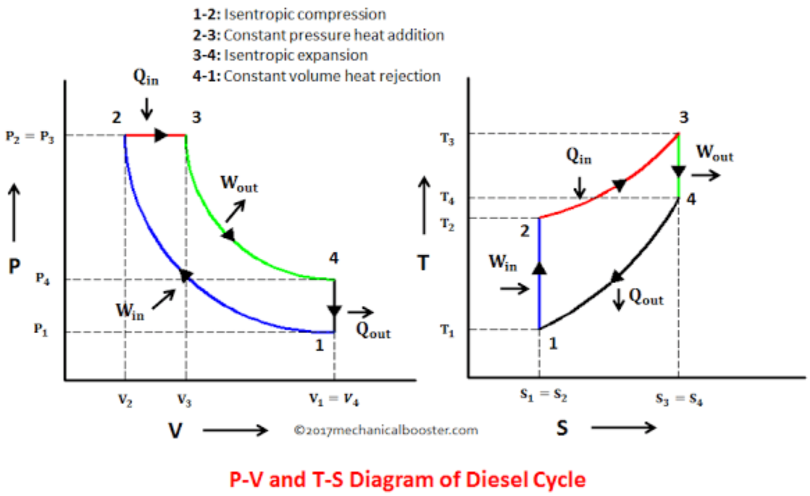


Figure 6: Property diagrams for the Diesel cycle.

The Brayton Cycle

The Brayton cycle is the ideal cycle for gas-turbine engines. It uses steady flow processes rather than closed system analysis. Combustion is replaced by constant-pressure heat addition from an external source, and exhaust is replaced by constant-pressure heat-rejection to ambient air.

The ideal Brayton cycle is represented by:

- An isentropic compression in a compressor;
- A constant-pressure heat addition;
- An isentropic expansion in a turbine;
- Constant-pressure heat rejection.

The pressure ratio describe the pressure after and before the isentropic compression:

$$r_p = \frac{P_2}{P_1}.$$

The thermal efficiency of the Brayton cycle is:

$$\eta_{\text{th,Brayton}} = 1 - \frac{1}{r_p^{(k-1)/k}}.$$

Recall that the isentropic efficiencies of the compressor and turbine are:

$$\eta_c \approx \frac{h_{2s} - h_1}{h_{2a} - h_1}, \quad \eta_t \approx \frac{h_3 - h_{4a}}{h_3 - h_{4s}}.$$

Lecture 20

2026-03-24

7.2 Vapour Power Cycles

The Carnot Vapour Cycle

The ideal Carnot vapour cycle is represented by:

- Isothermal heat addition in a boiler;
- Isentropic expansion in a turbine;
- Isothermal heat rejection in a condenser;
- Isentropic compression in a compressor.

This appears as a rectangle on a $T - s$ diagram. While the Carnot cycle is the most efficient cycle operating between two specified temperature limits, it is not a realistic model:

- From stage $1 - 2$, heat transfer is limited to a two-phase system which mean maximum $T_H = 374°$;
- From states $2 \to 3$, turbines cannot handle steam with a high moisture content as it results in erosion;
- From states $4 \to 1$, a compressor handling two phases is impractical.

The Rankine Cycle

The Rankine cycle is a much more realistic ideal vapour cycle for plants. It is internally reversible. The ideal Rankine vapour cycle is represented by:

- Isentropic compression in a pump;
- Constant pressure heat addition in a boiler;

- Isentropic expansion in a turbine;
- Constant pressure heat rejection in a condenser.

Note that the actual vapour power cycle has internal irreversibility, like fluid friction and heat loss to surroundings. If we try and increase the efficiency of the Rankine cycle, we can either:

- Increase the average temperature in the boiler;

Super heating the steam to higher temperatures in the boiler both increases the work output (and heat input) and decreases the moisture content at the final state of the turbine. The efficiency does see a net increase since the average temperature at which heat is added is increased. However, when the steam gets too hot, it can damage equipement ($\sim 620°C$).

Alternatively, increasing the boiler pressure will shift the Ts graph to the left. This increases the average boiler temperature, but will also increase the moisture content at the final turbine state. This can be corrected by reheating the steam, expanding it twice! In theory, adding infinite reheats approaches an isothermal, and therefore ideal process, but in reality, anything beyond a second reheat is not practical. The optimal reheat cycle pressure is about $\frac{1}{4}$ of the maximum cycle pressure.

- Decrease the average temperature in the condenser.

Note that lowering the condenser pressure lowers the $T_{\text{low,avg}}$ in the condenser, increasing the efficiency at the cost of increasing the moisture content of the steam at the final stage of the turbine. Think of this as 'lowering the floor' on the $T-s$ diagram, meaning the final state of the isentropic expansion in the turbine reaches below the vapour line into $x < 1$.

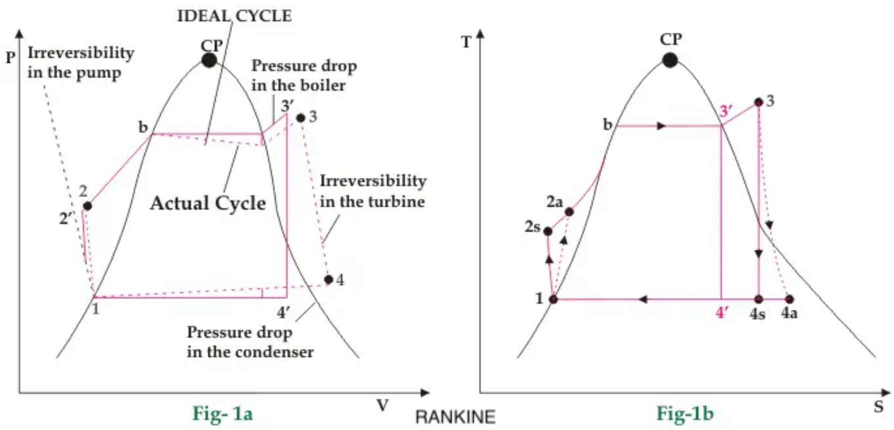


Figure 7: The ideal and real Rankine cycle, with no reheating stage.

Example. Consider a steam power plant operating on the simple ideal Rankine cycle. Steam enters the turbine at $3MPa$ and $350°C$ and is condensed in the condenser at $75kPa$.

To find the thermal efficiency, we need $w_{\text{net,out}}$, q_{in}. To find w_{out} generated by the turbine, we consider that from state $3 \to 4$, we have an isentropic expansion between our two given states. Using $\Delta s = 0$ and finding our initial entropy, we confirm that state 4 is a saturated mixture at $75kPa$. We can apply our steady flow energy balance for a turbine:

$$Q_{in} - W_{out} = \Delta H.$$

Where we drop Q_{in} as it is an isentropic process ($\implies$ adiabatic and reversible).

To find w_{in}, we can do a similar analysis on the pump, notably using:

$$w_{in} = h_2 - h_1 = \nu_1 (P_2 - P_1) .$$

Via flow work.

Lastly, to find q_{in}, we analyse state $2 \to 3$, the constant pressure heat addition in the boiler.

$\Diamond$

Lecture 22

2026-03-31

Heat pumps and refrigerators are analogous as they both transfer heat from low temperature to high temperature, however they differ in their goals. Refrigerators have Q_L as their desired output, while heat pumps have Q_H.

$$\begin{aligned} \text{COP}_R &= \frac{\text{cooling}}{\text{work input}} = \frac{Q_L}{W_{\text{net,in}}} \\ \text{COP}_{HP} &= \frac{\text{heating}}{\text{work input}} = \frac{Q_H}{W_{\text{net,in}}}. \end{aligned}$$

We maintain the identity $\text{COP}_{HP} = \text{COP}_R + 1$.

Consider the Carnot cycle, but in reverse. Recall that the Carnot cycle defines the most efficient (highest COP) operation between two temperatures, and is fully reversible.

- Constant temperature heat addition;
- Isentropic compression in compressor;
- Constant temperature heat rejection;
- Isentropic expansion in turbine.

Traversing the Carnot cycle in reverse, or counter-clockwise around a $P - \nu$ or $T - s$ diagram, will use net work in to transfer heat from a low temperature reservoir to a high temperature reservoir. As such, when we assume a reversible cycle, we can replace Q_L with T_L and Q_H with T_H.

$$\begin{aligned} \text{COP}_R &= \frac{T_L}{T_H - T_L} = \frac{1}{T_H/T_L - 1} \\ \text{COP}_{HP} &= \frac{T_H}{T_H - T_L} = \frac{1}{1 - T_L/T_H}. \end{aligned}$$

Even though this describes the most efficient refrigeration cycle, it is not realistic. Process $2 \to 3$ involves compression of a liquid-vapour mixture, requiring a compressor that can withstand two phases and will corrode. Additionally, the expansion of a high-moisture-content refrigerant in a turbine for $4 \to 1$ is also susceptible to degradation.

Vapour-Compression Refrigeration Cycle

The ideal model for refrigeration cycle involves a refrigerant that is completely vaporized before compression. Additionally, we replace the compressor with a throttle. We can do this since the goal of our cycle is not work out! This gives:

- Isentropic compression in compressor;
- Constant-pressure heat rejection in a condenser;
- Throttling for pressure drop;
- Constant-pressure heat absorption in an evaporator.

On a $T-s$ diagram, it looks very similar to our Rankine cycle in reverse. However, our pressure drop is not isentropic, and therefore not reversible. This is a more realistic process compared to the impracticality of a ‘reversible’ turbine.

In a real-life vapour-compression refrigeration cycle, fluid friction and heat transfer further lower the COP. We obtain things like non-isentropic compression, superheated vapour after the evaporator, pressure drops in condenser and evaporator, etc.

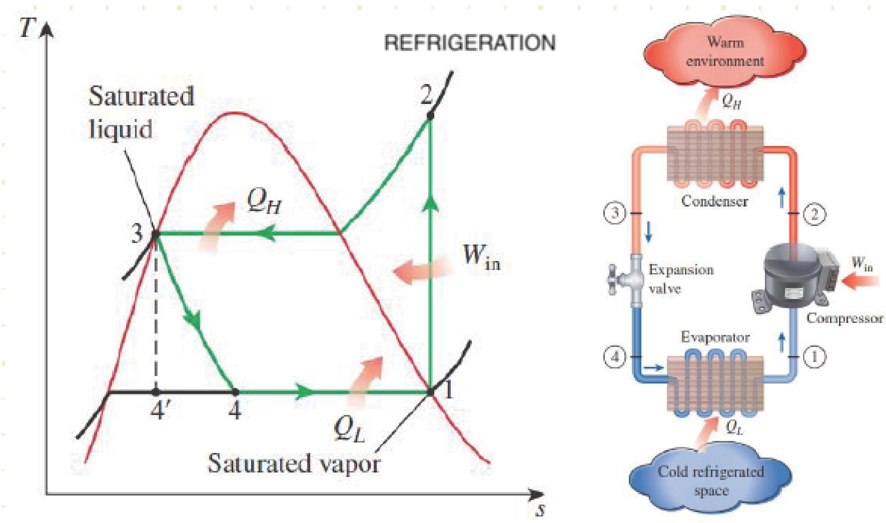


Figure 8: A T-s diagram of the ideal steady-flow vapour-compression refrigeration cycle.

There are several options for refrigerants, notably chlorofluorocarbons (toxic CFCs), ammonia, or R-134a. All of which are dangerous or toxic in some form, whether to humans or the ozone layer.

- R-11 is used in large capacity water chillers in buildings;
- R-134a, which replaced R-12 is used domestically;
- R-ww is bad for the ozone layer and is being replaced from many devices.

Heat pumps however, rely on air-to-air systems, or geothermal (water as a source) system.