Thermodynamics

1. Thermodynamic processes can be:

   ○ **isothermal processes**, $\Delta T = 0$ (so $P \sim 1/V$);

   ○ **isobaric processes**, $\Delta P = 0$ (so $T \sim V$);

   ○ **isovolumetric or isochoric processes**, $\Delta V = 0$ (so $T \sim P$);

   ○ **adiabatic processes**, $\Delta Q = 0$ (so $P \sim 1/V^{\gamma}$);

   ○ **cyclic processes**, *all* state variables (P, V, T, E, S) return to their original values after each cycle.

   (Throughout, we will assume the processes involve an ideal gas with constant n.)

   In a cyclic process, the state variables all return to their initial values after one cycle.

2. Thermodynamical systems are often described using **PV diagrams**, with pressure plotted on the vertical axis and volume plotted on the horizontal axis. In such a diagram, the area under a curve is easily related to work:
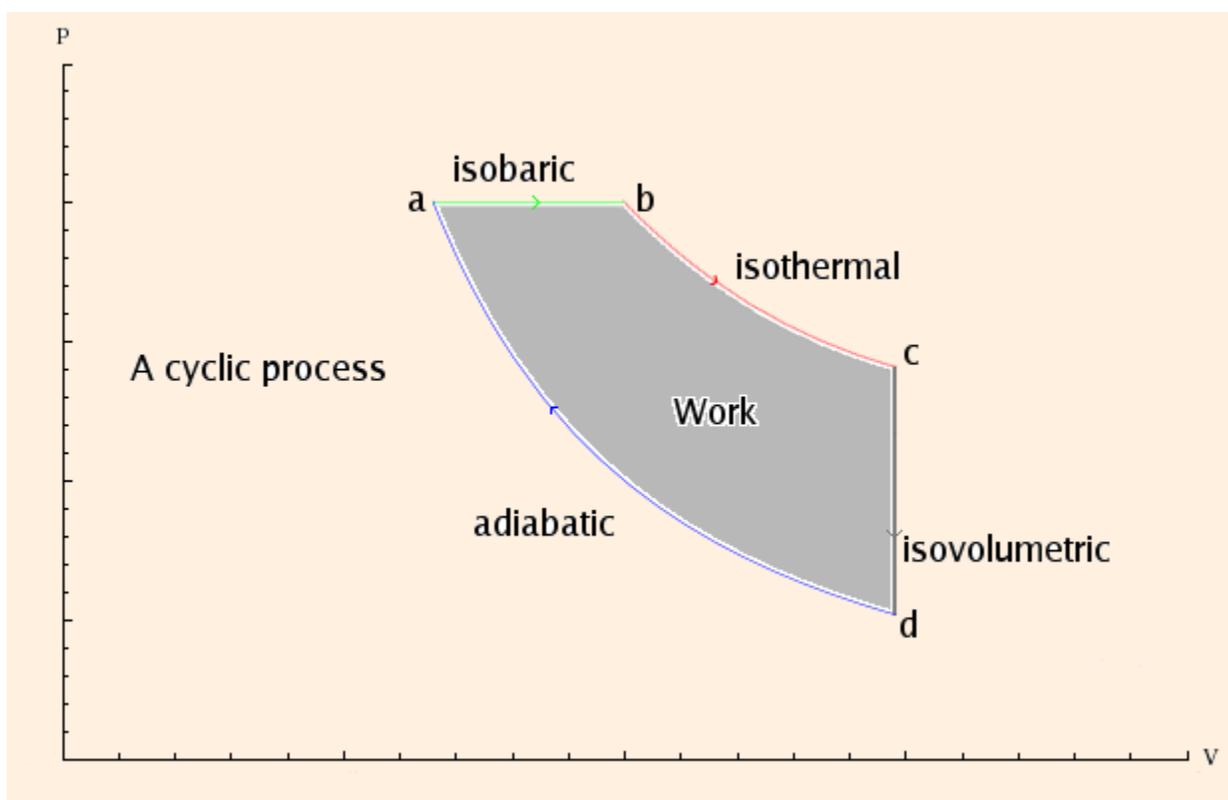
   Assuming this PV diagram describes a process involving an ideal gas, we can deduce the following:

as a→b	$P_a = P_b$	$\Delta E_{a \to b} = n\, c_v\, (T_b - T_a)$	$\Delta Q_{a \to b} = n\, c_p\, (T_b - T_a)$	$W_{a \to b} = -P_a\,($

at b	$T_b = P_b V_b / (n R)$	$T_b > T_a$	$\Delta Q_{a \to b} > 0$	$W_{a \to b} < 0$
as b→c	$T_b = T_c$	$\Delta E_{b \to c} = 0$	$\Delta Q_{b \to c} = -W_{b \to c}$	$W_{b \to c} = -n R$
at c	$T_c = P_c V_c / (n R)$		$\Delta Q_{b \to c} > 0$	$W_{b \to c} < 0$
as c→d	$V_c = V_d$	$\Delta E_{c \to d} = n c_v (T_d - T_c)$	$\Delta Q_{c \to d} = n c_v (T_d - T_c)$	$W_{c \to d} = 0$
at d	$T_d = P_d V_d / (n R)$	$T_d < T_c$	$\Delta Q_{c \to d} < 0$	
as d→a	$P_d V_d^{c_p/c_v} = P_a V_a^{c_p/c_v}$	$\Delta E_{d \to a} = n c_v (T_a - T_d)$	$\Delta Q_{d \to a} = 0$	$W_{d \to a} = n c_v$
at a	$T_a = P_a V_a / (n R)$	$T_a > T_d$		$W_{d \to a} > 0$

In addition, we know that $\Delta E_{a \to b} + \Delta E_{c \to d} + \Delta E_{d \to a} = 0$, but in this case it only tells us that $T_b = T_c$.

From this we can compute the total heat added during the cycle:

$$n c_p (T_b - T_a) + n R T_b \ln (V_c / V_b)$$

and the total work done by the gas:

$$P_a (V_b - V_a) + n R T_b \ln (V_c / V_b) - n c_v (T_a - T_d),$$

corresponding to the shaded area in the PV diagram.

> Note that heat enters this "engine" in steps a→b and b→c, and exits it in step c→d; the total work done by the engine is positive. If the cycle were operated in reverse, it would be a "refrigerator", taking heat from a cooler environment during step d→c and exhausting it to a warmer environment from c→a; the total work done by the refrigerator is negative. The meaning of this is that it requires external work to move heat from a cooler to a warmer place.

3. To see how this information is applied to a problem, consider the following thermodynamic cycle for n = 4 moles of a monatomic ideal gas:
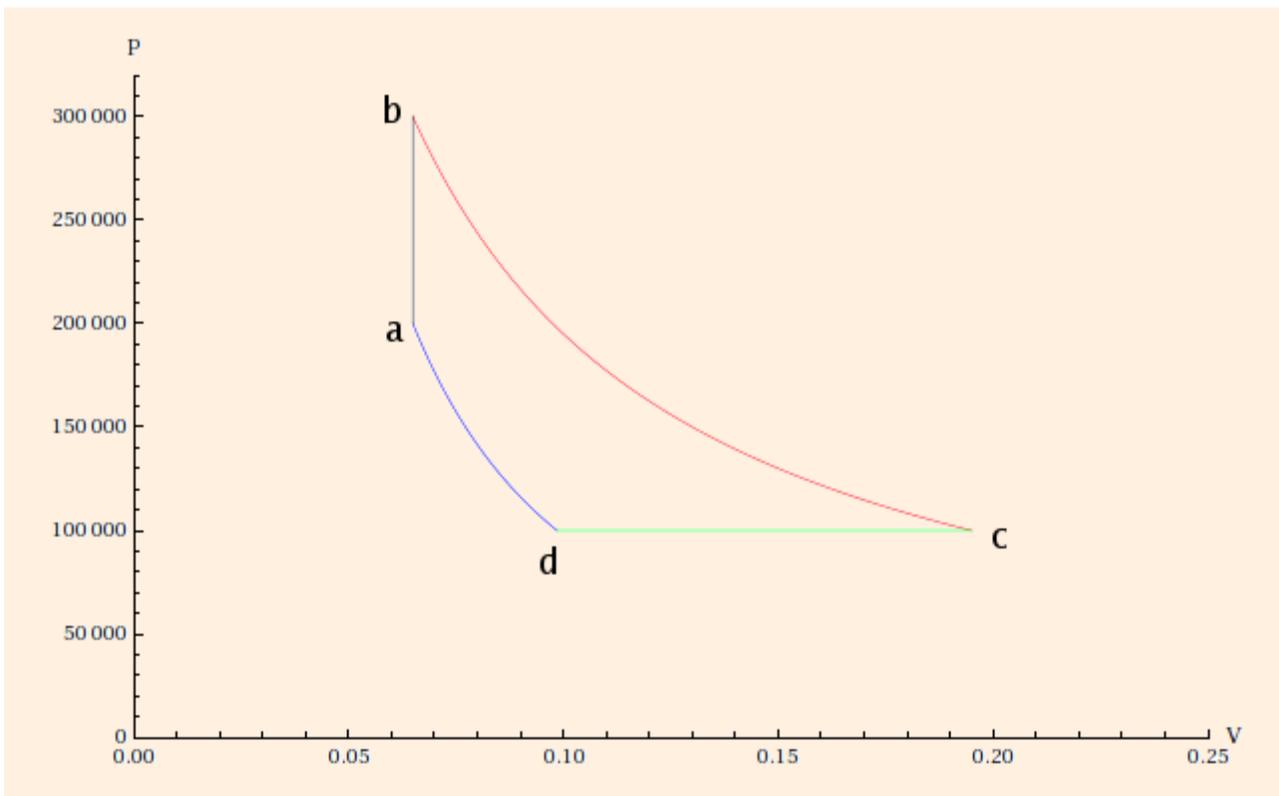
1. from a to b, the system undergoes an isovolumetric increase in pressure;
2. from b to c, the system undergoes an isothermal expansion;
3. from c to d, the system undergoes an isobaric compression;
4. from d to a, the system undergoes an adiabatic compression.

Suppose we are given P_a = 200,000 Pa, P_b = 300,000 Pa, P_c = 100,000 Pa and V_a = 65 L.

We know that $P_d = P_c$, $V_b = V_a$, and $T_b = T_c$. We can use the ideal gas law to compute the temperatures at points a and b from the pressure and volumes at those points: 390.907 K and 586.36 K, respectively. From the latter we can compute the volume at point c, which is 195 L.

We can use the adiabatic equation for an ideal gas:

$$P_d \, V_d^{\gamma} = P_a \, V_a^{\gamma},$$

to compute V_d = 98.5216 L. Finally, we can use the ideal gas law to find that T_d = 296.252 K.

Since b to c is an isothermal expansion, the first law tells us that $\Delta Q_{b \to c} = - \Delta W_{b \to c}$. Using the ideal gas law, we find

$$\Delta W_{b \to c} = - \int_b^c P \, dV$$

$$= - n \, R \, T_b \int_b^c dV / V$$

$$= - n \, R \, T_b \ln (V_c / V_b) = -21,422.9 \text{ J}.$$

(Note the sign: the gas does external work.)

Using the equations for isovolumetric and isobaric processes, we have

$$\Delta Q_{a \to b} = n\, c_v\, (T_b - T_a) \qquad \Delta Q_{b \to c} = n\, R\, T_b \ln(V_c / V_b) \qquad \Delta Q_{c \to d} = n\, c_p\, (T_d - T_c)$$
$$= 9750\text{ J} \qquad\qquad\qquad = 21{,}422.9\text{ J} \qquad\qquad\qquad =-24{,}119.6\text{ J}$$

Finally, consistent with the fact that $\Delta E = 0$ for a cycle, we compute

$$\Delta W_{a \to b} = 0 \quad \Delta W_{b \to c} = -\,n\, R\, T_b \ln(V_c / V_b) \qquad \Delta W_{c \to d} = P_c\,(V_c - V_d) \qquad \Delta W_{d \to a} = c_v\,(P_a\, V_a$$
$$= -21{,}422.9\text{ J} \qquad\qquad = 9647.84\text{ J} \qquad\qquad = 4721$$

4. The **efficiency** of an engine is

$$\varepsilon = W / Q_h$$

$$= (Q_h - Q_c) / Q_h$$

$$= 1 - Q_c / Q_h.$$

Here, energy is taken in as Q_h, work W is done by the engine, and the waste heat is discharged as Q_c.

In the example above, $Q_h = 31{,}172.9$ J, $W = 7053.33$ J, $Q_c = 24{,}119.6$ J and $\varepsilon = 22.6265\%$.

This calculation obscures some interesting facts:

- for this cycle, as the number of degrees of freedom of the gas $\chi \to \infty$ (with all other values unchanged), $\varepsilon \to 0$ as $1/\chi$ (more heat must be removed during isobaric cooling to lower the temperature the same amount, because more of the heat comes from non-translational degrees of freedom which do not affect temperature);

- ε does not depend on n; increasing n will only lower the temperatures (via the ideal gas law; with more molecules, less energy is available per molecule);

- while the efficiency is a complicated function of the given values, it is turns out that, holding all other values constant, increasing P_b or decreasing P_c will increase ε, while the value of V_a does not alter ε at all and the chosen value of P_a is almost optimal.

Of course, for another cycle, the results can be *very* different.

For an air conditioner, **heat pump** in air conditioning mode, or refrigerator, $\varepsilon = Q_{transferred} / W_{required}$. The efficiency of a refrigerator can be greater than 1, since

$$\varepsilon = Q_c / (Q_h - Q_c)$$

$$= 1 / (Q_h / Q_c - 1),$$

where Q_c is the heat removed from the cooler environment and Q_h is the heat exhausted into the warmer environment. Note that Q_h must be greater than Q_c.

5. We often consider a cycle operating between two **heat reservoirs** (of infinite heat capacity), one at temperature $T_{h(ot)}$ and the other at temperature $T_{c(old)}$. For such a device, $\underline{\Delta S}$ includes the engine itself *and* the reservoirs. Since the engine operates in a cycle, its $\underline{\Delta S}$ is 0, so for isothermal transfers,

$$\Delta S = - \Delta Q_h / T_h + \Delta Q_c / T_c.$$

In general, $\Delta S = \int dQ / T$.

For the example above, $\Delta S_{b \to c} = 36.5355$ J/K, and of course $\Delta S_{d \to a} = 0$. To compute $\Delta S_{a \to b}$ and $\Delta S_{c \to d}$, we use the ideal gas law to express T as a function of P and V:

$$\Delta S_{a \to b} = \int n\, c_v\, dT / T$$

$$= \int n\, c_v\, (V\, dP / (n\, R)) / (P\, V / (n\, R))$$

$$= n\, c_v\, \ln (P_b / P_a) = 20.2262 \text{ J/K}$$

and

$$\Delta S_{c \to d} = \int n\, c_p\, dT / T$$

$$= \int n\, c_p\, (P\, dV / (n\, R)) / (P\, V / (n\, R))$$

$$= n\, c_p\, \ln (V_d / V_c) = -56.7617 \text{ J/K}$$

The changes in entropy of the reservoirs are of course dependent on their temperatures. Assuming that the isobaric compression lost heat to a reservoir at room temperature ($< T_d$), and that the isochoric and isothermal processes gained heat from a reservoir at 320 C ($> T_b$),

$$\Delta S_{\text{cold reservoir}} = 24119.6 / 293.15 \text{ J/K} = 82.277 \text{ J/K and}$$

$$\Delta S_{\text{hot reservoir}} = -31172.9 / 593.15 \text{ J/K} = -52.555 \text{ J/K,}$$
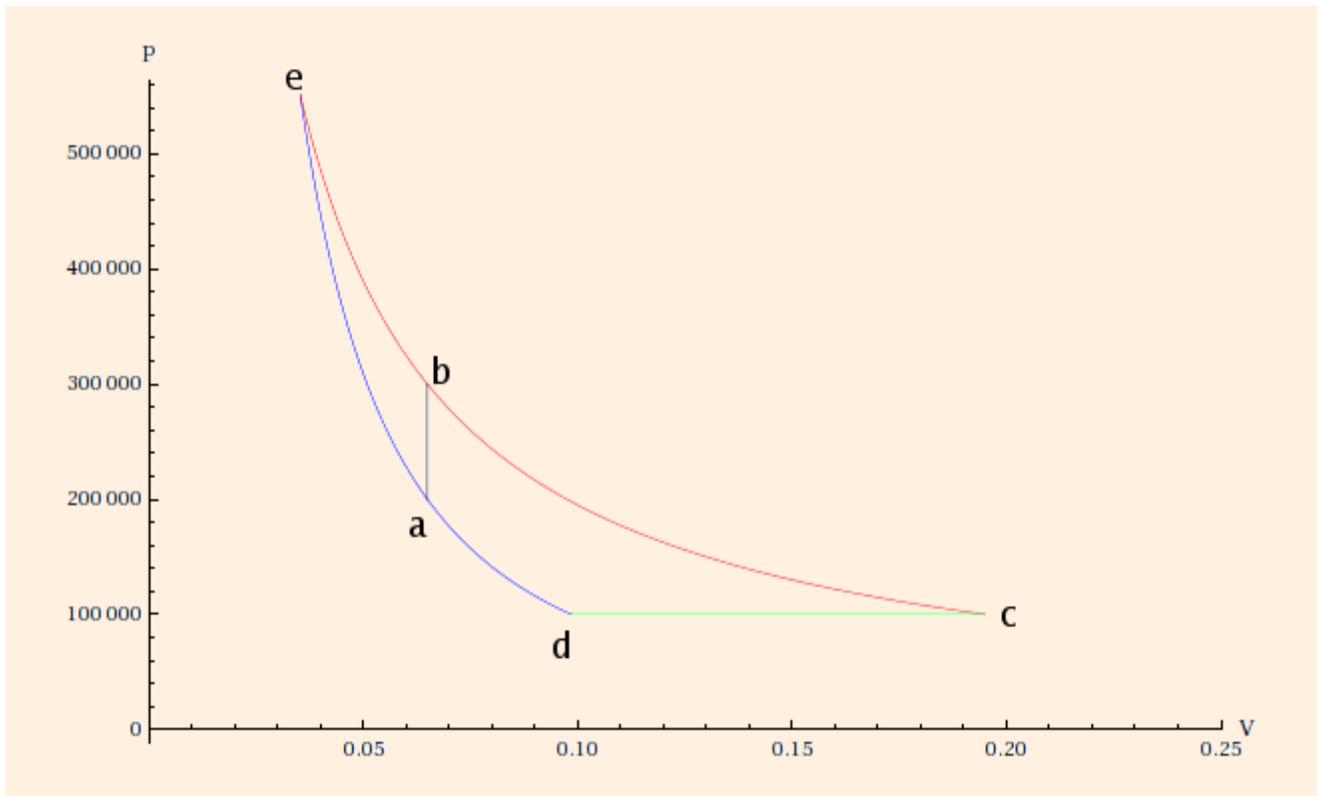
so that

$$\Delta S_{\text{reservoirs}} = 29.722 \text{ J/K,}$$

which is greater than zero, as required by the second law of thermodynamics.

If we did not know T as a function of P and V, it would be necessary to connect each pair of endpoints with a combination of adiabatic and isothermal processes, and compute the change in entropy using

those new processes. For example:

Process a→e is an adiabatic process, and e→b is isothermal. $P_e = 551,135$ Pa and $V_e = 35.3815$ L, from

$$P_a \, V_a^{\,\gamma} = P_e \, V_e^{\,\gamma}$$

$$= n \, R \, T_b \, V_e^{\,\gamma - 1}$$

This gives us (using the same equations as above)

$$\Delta Q_{a \to e} = 0 \text{ and}$$

$$\Delta Q_{e \to b} = 11{,}859.9 \text{ J}.$$

Since entropy is a state variable,

$$\Delta S_{a \to b} = \Delta S_{e \to b} = 20.2262 \text{ J/K},$$

as before. Either way, the entropy change *of the engine* is zero, because it is a cycle: all state variables, including entropy, end at the same state in which they began. Therefore $\Delta S_{c \to d} = -56.7617$ J/K.

6. The **Carnot cycle** is the most efficient cyclic thermodynamic process conceivable:

    1. isothermal expansion, with $\Delta Q = Q_h$ at T_h ;
    2. adiabatic expansion, with $T_h \to T_c$;

3. isothermal compression, with $\Delta Q = - Q_c$ at T_c ; and

4. adiabatic compression, with $T_c \rightarrow T_h$.

What makes it so is that each step of the Carnot cycle is **reversible**: all changes of state are infinitesimally close to equilibrium.

Reversible changes of state are infinitely long; all real changes of state are irreversible.

In isothermal processes, by definition the gas is in thermal equilibrium with the reservoir. An adiabatic process can be irreversible:

Consider a closed, thermally insulated volume with a partition in the middle, such that nearly all of the gas molecules are on one side of the partition; the other side is a nearly perfect vacuum. With removal of the partition, the gas adiabatically but irreversibly doubles in volume.

A reversible adiabatic process would be a change in volume by infinitesimal steps while the gas is thermally insulated.
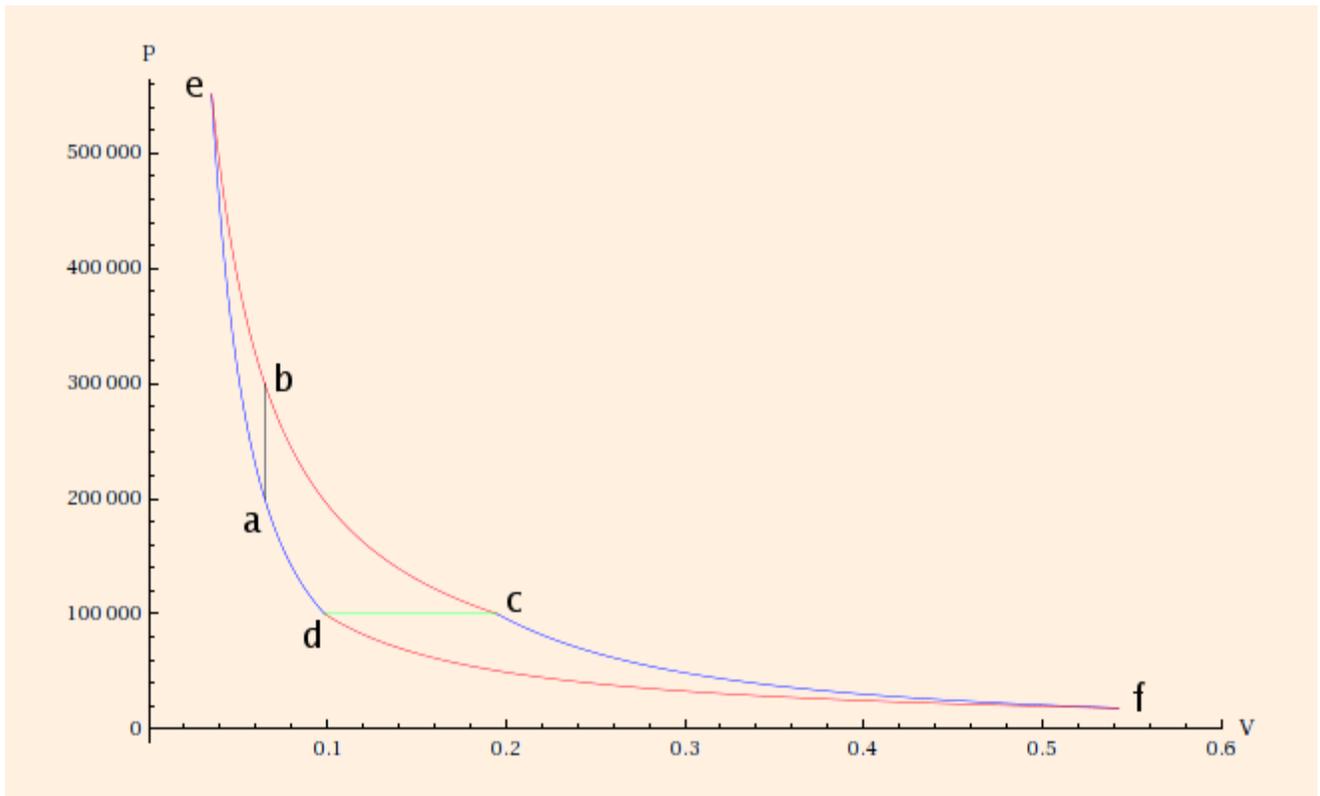
Since it is reversible, the total entropy change of the Carnot cycle reservoirs is zero. This gives us

$$0 = - Q_h / T_h + Q_c / T_c$$

or

$$Q_c / Q_h = T_c / T_h.$$

If we attempt to compute the entropy change for c→d by finding a point f on the PV diagram such that c→f is adiabatic and f→d is isothermal, we find that we have constructed a Carnot cycle:

Hence the total entropy change is zero *including the reservoirs*, and its efficiency is

$$1 - T_d / T_b = 49.4761\%.$$

The efficiency of a Carnot Refrigerator is $T_c / (T_h - T_c)$.

7. Thermodynamic cycles of practical interest include:

   ○ the **Diesel Engine**, consisting of adiabatic compression (a → b), isobaric heating (b → c), adiabatic expansion (c → d) and isovolumetric cooling (d → a);

   $$\varepsilon = 1 - (T_d - T_a) / ((1 + 2 / \chi) (T_c - T_b))$$

   ○ the **Otto Cycle**, consisting of adiabatic compression, isovolumetric heating, adiabatic expansion and isovolumetric cooling;

   $$\varepsilon = 1 - (V_{small} / V_{large})^{(2 / \chi)}$$

   ○ the **Stirling Engine**, consisting of alternating isothermal and isovolumetric processes.

   $$\varepsilon = 1 / (1 + T_{lower} / |\Delta T| + \chi / (2 \ln (V_{large} / V_{small})))$$

In each case, ε was computed for an ideal gas. Note that in each case, it is independent of n, and increases with decreasing χ. This generalizes what we saw above: if we think of work as the result of increased temperature, less heat input is required to change the temperature of a gas with fewer degrees of freedom.

8. It is important to remember that these are *models* of real thermodynamic process. In actual physical processes,

   ○ gasses are *never* perfectly ideal;
   ○ n is *never* constant;
   ○ *nothing* has infinite heat capacity; and
   ○ *no* process is perfectly adiabatic (or, of course, reversible).

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