THERMODYNAMICS: COURSE INTRODUCTION

Course Learning Objectives:

To be able to use the First Law of Thermodynamics to estimate the potential for thermo-mechanical energy conversion in aerospace power and propulsion systems.

Measurable outcomes (assessment method):

1) To be able to state the First Law and to define heat, work, thermal efficiency and the difference between various forms of energy. (quiz, self-assessment, PRS)

2) To be able to identify and describe energy exchange processes (in terms of various forms of energy, heat and work) in aerospace systems. (quiz, homework, self-assessment, PRS)

3) To be able to explain at a level understandable by a high school senior or non-technical person how various heat engines work (e.g. a refrigerator, an IC engine, a jet engine). (quiz, homework, self-assessment, PRS)

4) To be able to apply the steady-flow energy equation or the First Law of Thermodynamics to a system of thermodynamic components (heaters, coolers, pumps, turbines, pistons, etc.) to estimate required balances of heat, work and energy flow. (homework, quiz, self-assessment, PRS)

5) To be able to explain at a level understandable by a high school senior or non-technical person the concepts of path dependence/independence and reversibility/irreversibility of various thermodynamic processes, to represent these in terms of changes in thermodynamic state, and to cite examples of how these would impact the performance of aerospace power and propulsion systems. (homework, quiz, self-assessment, PRS)

6) To be able to apply ideal cycle analysis to simple heat engine cycles to estimate thermal efficiency and work as a function of pressures and temperatures at various points in the cycle. (homework, self-assessment, PRS)

Teaching & Learning Methods

1) Detailed lecture notes are available on the web (for viewing and/or downloading). You should download a copy of these and bring them with you to lecture.

2) Preparation and participation will be important for learning the material. You will be responsible for studying the notes prior to each lecture. Several reading
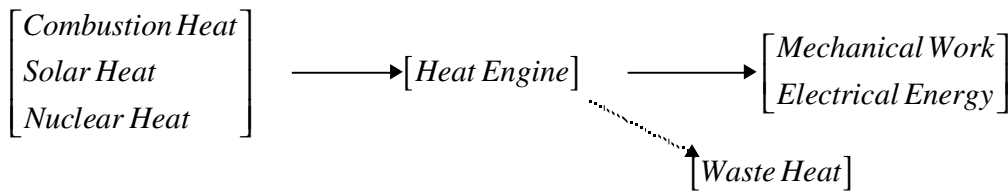
<u>assignments</u> will be given to help promote this activity (1/3 of participation grade).

3) Several active learning techniques will be applied on a regular basis (turn-to-your-partner exercises, muddiest part of the lecture, and ungraded concept quizzes). We will make extensive use of the PRS system (2/3 of participation grade).

4) Homework problems will be assigned (approximately one hour of homework per lecture hour). The Unified Engineering collaboration rules apply.
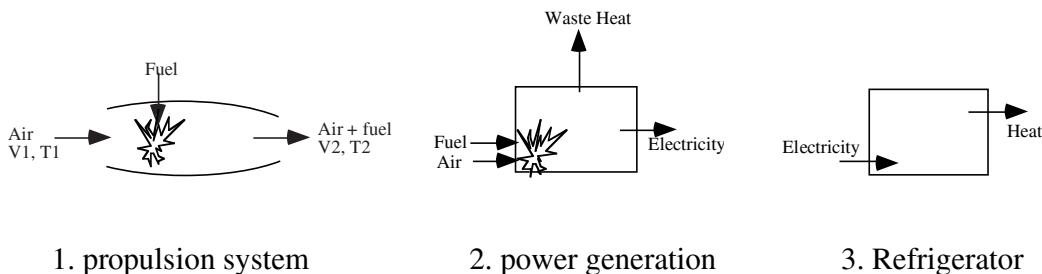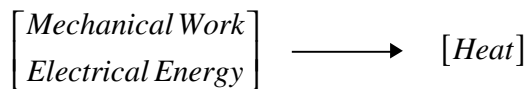
THERMODYNAMICS CONCEPTS

I.   Thermodynamics (VW, S & B: Chapter 1)

A. Describes processes that involve changes in temperature, transformation of energy, relationships between heat and work.

B. It is a science, and more importantly an engineering tool, that is necessary for describing the performance of propulsion systems, power generation systems, refrigerators, fluid flow, combustion, ...

C. Generalization of extensive empirical evidence (however most thermodynamic principles and can be derived from kinetic theory)

D. Examples of heat engines

$$\begin{bmatrix} Combustion\,Heat \\ Solar\,Heat \\ Nuclear\,Heat \end{bmatrix} \longrightarrow [Heat\,Engine] \longrightarrow \begin{bmatrix} Mechanical\,Work \\ Electrical\,Energy \end{bmatrix}$$

$$[Waste\,Heat]$$

OR

$$\begin{bmatrix} Mechanical\,Work \\ Electrical\,Energy \end{bmatrix} \longrightarrow [Heat]$$

1. propulsion system   2. power generation   3. Refrigerator

## E. Questions:

1. Describe the energy exchange processes in _____ (fill in the blank, e.g. a nuclear power plant, a refrigerator, a jet engine).

2. Given that energy is conserved, where does the fuel+oxidizer energy that is used to power an airplane go?

3. Describe the energy exchange processes necessary to use electricity from a nuclear power plant to remove heat from the food in a refrigerator.

4. Describe the energy exchange processes necessary for natural gas to be used to provide electricity for the lights in the room you are in.

II. Concept of a thermodynamic system *(VW, S & B: 2.1)*

A. A quantity of matter of fixed identity, boundaries may be fixed or movable, can transfer heat and work across boundary but not mass
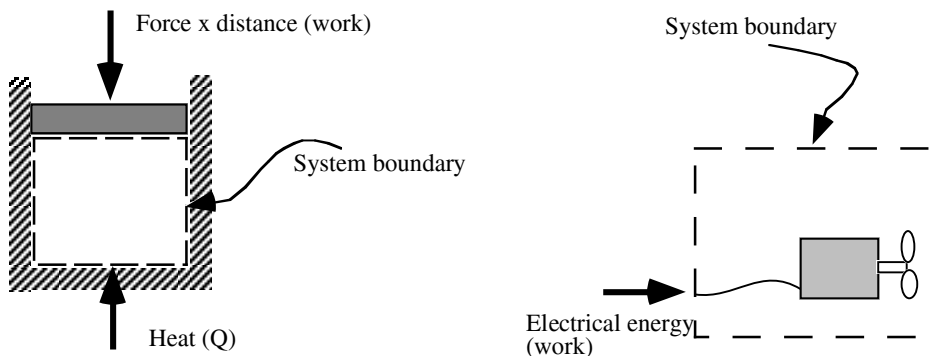

B. Identifiable volume with <u>steady flow</u> in and out, a control volume. Often more useful way to view devices such as engines
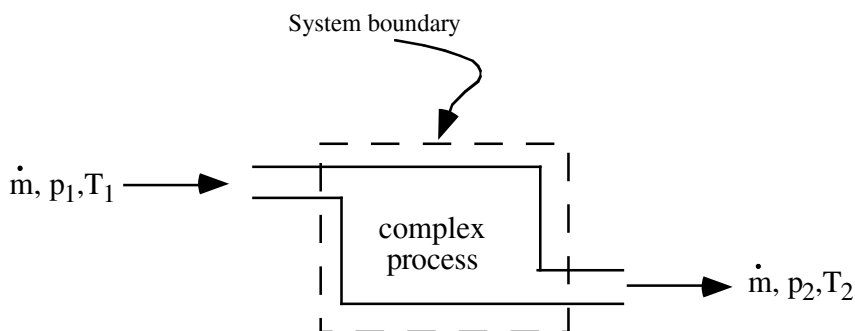
III. Thermodynamic state of a system

A. The thermodynamic state of a system is defined by specifying a set of measurable properties sufficient so that all remaining properties are determined. Examples of properties: pressure, temperature, density, internal energy, enthalpy, and entropy.

B. For engineering purposes we usually want gross, average, macroscopic properties (not what is happening to individual molecules and atoms) thus we consider substances as continua -- the properties represent averages over small volumes. For example, there are 10^{16} molecules of air in 1 mm^3 at standard temperature and pressure. *(VW, S & B: 2.2)*

. Intensive properties do not depend on mass (*e.g.* p, T, ρ, v=1/ρ, u and h); extensive properties depend on the total mass of the system (*e.g.* V, M, U and H). Uppercase letters are usually used for extensive properties. *(VW, S & B: 2.3)*

D. Equilibrium: States of a system are most conveniently described when the system is in equilibrium, *i. e.* it is in steady-state. Often we will consider processes that change "slowly" -- termed quasi-steady. *(VW, S & B: 2.3-2.4)*
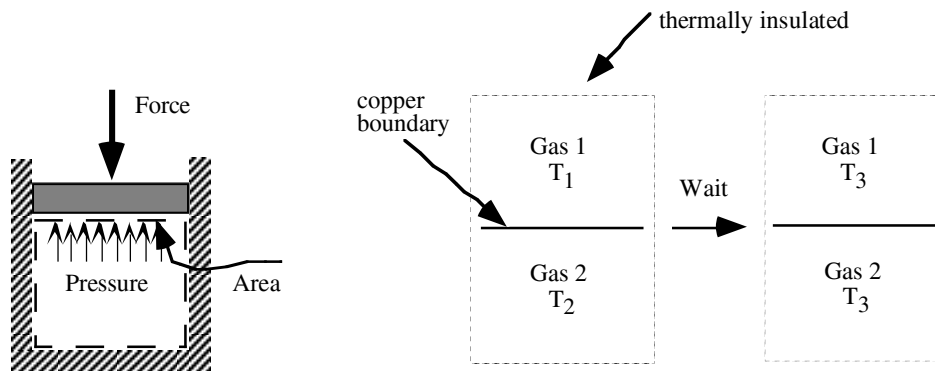
1. mechanical equilibrium
(force balances pressure times area)

2. thermal equilibrium
(same temperature)

E. Two properties are needed to define the state of any pure substance undergoing a steady or quasi-steady process. (This is an experimental fact!) *(VW, S & B: 3.1, 3.3)*

1. For example for a thermally perfect gas (this is a good engineering approximation for many situations, but not all (good for $p \ll p_{crit}$, and $T > 2T_{crit}$ up to about $4p_{crit}$). *(VW, S & B: 3.4)*:

$$p\,\overline{v} = \mathcal{R}T$$

$\overline{v}$ is volume per mol of gas, $\mathcal{R}$ is the universal gas constant $\mathcal{R} = 8.31 \text{kJ/Kmol-K}$. Dividing by molecular weight,

$$p\,\overline{v}/\mathcal{M} = (\mathcal{R}/\mathcal{M})\,T$$

where $\mathcal{M}$ is the molecular weight of the gas. Most often written as

$$pv = RT \ \text{ or } p = \rho RT$$

where v is the specific volume and R is the gas constant (which varies depending on the gas. $R = 287 \text{J/kg - K}$ for air).

Thus, if we know p and T we know ρ, if we know T and ρ, we know p, *etc*.

F. For thermodynamic processes we are interested in how the state of a system changes. So typically we plot the behavior as shown below. It is useful to know what a constant temperature line (isotherm) looks like on a p-v diagram, what a constant volume line (isochor) looks like on a T-p diagram, *etc*.
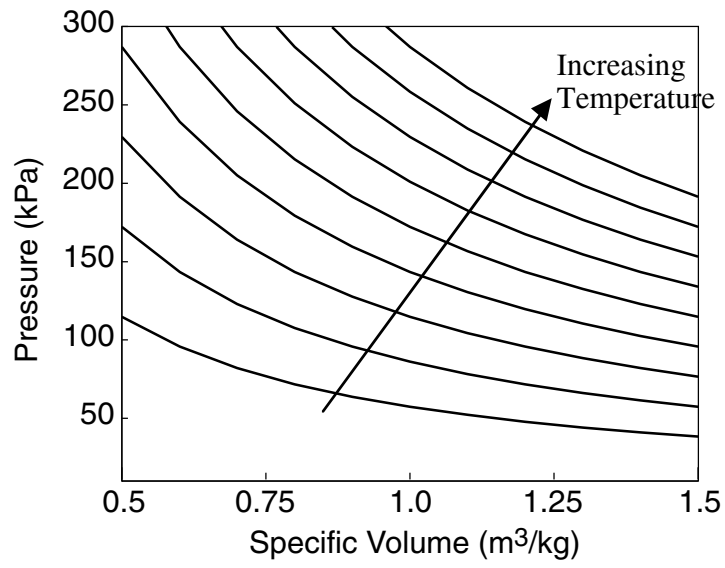
1. p-v diagram
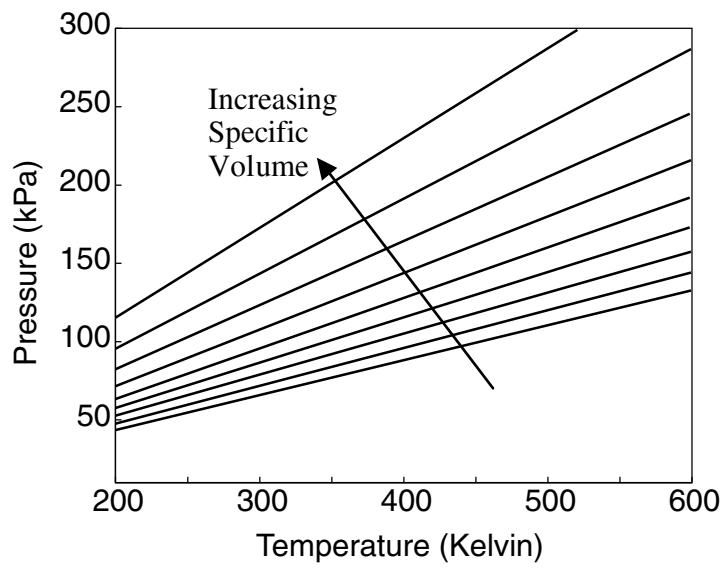
2. p-T diagram
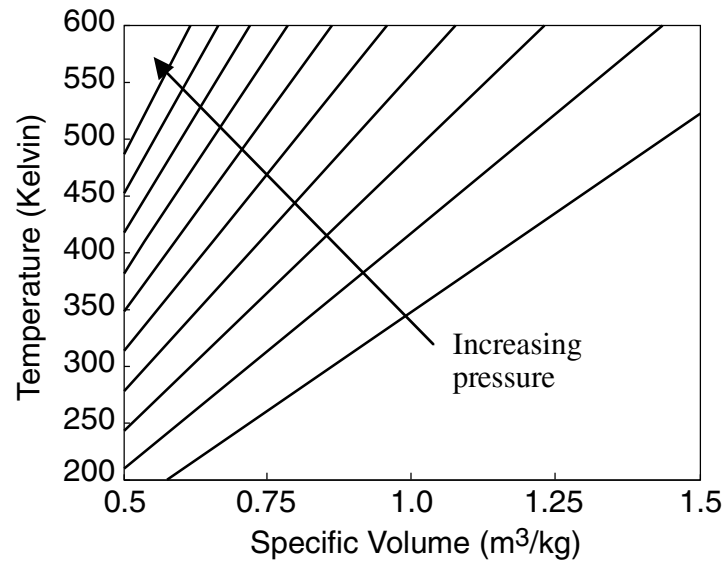
3. T-v diagram

G. Note that real substances may have phase changes (water to water vapor, or water to ice, for example). Many thermodynamic devices rely on these phase changes (liquid-vapor power cycles are used in many power generation schemes, for example). You will learn more about these in 16.050. In this course we will deal only with single-phase thermodynamic systems.
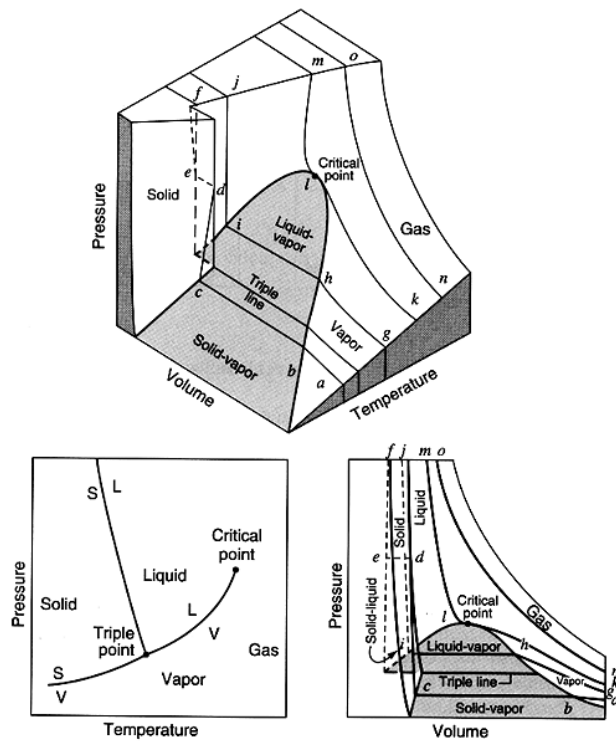
Pressure-temperature-volume surface for a substance that expands on freezing
(from *VW, S & B: 3.7*)

CHANGING THE STATE OF A SYSTEM WITH HEAT AND WORK

- Changes in the state of a system are produced by interactions with the environment through <u>heat</u> and <u>work</u>.

- During these interactions, equilibrium (a static or quasi-static process) is necessary for the equations that relate system properties to one-another to be valid.
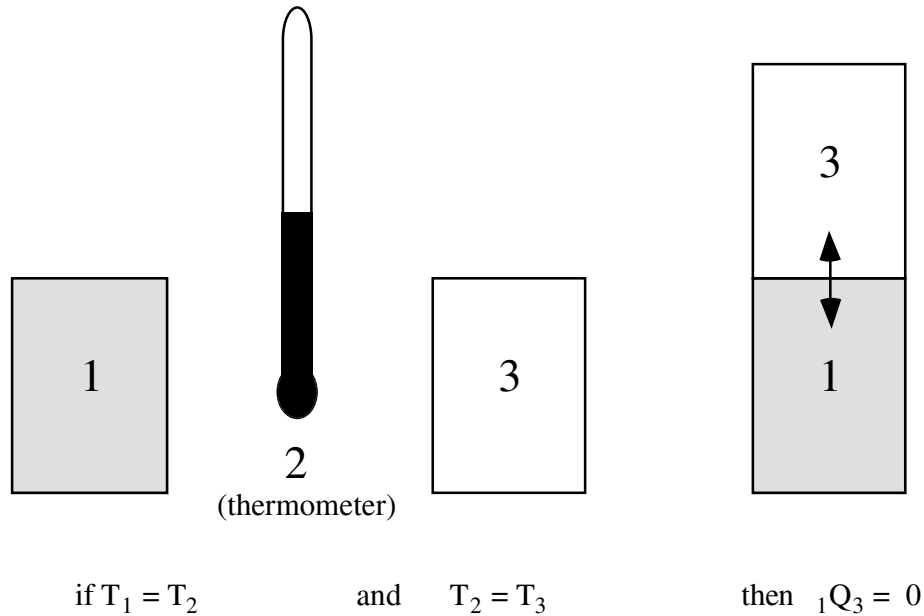
I. Changing the State of a System : Heat *(VW, S & B: 4.7-4.9)*

A. Heat is energy transferred between a system and its surroundings by virtue of a temperature difference only.

1. This transfer of energy can change the state of the system.

2. "<u>Adiabatic</u>" means no heat is transferred.

B. Zeroth Law of Thermodynamics *(VW, S & B: 2.9-2.10)*

1. There exists for every thermodynamic system in equilibrium a property called temperature. (Absolute temperature scales: $K = 273.15 + {}^{o}C$, $R = 459.9 + {}^{o}F$)

2. Equality of temperature is a necessary and sufficient condition for thermal equilibrium, *i.e.* no transfer of heat.

if $T_1 = T_2$ and $T_2 = T_3$ then $_1Q_3 = 0$

II.   Changing the State of a System: Work *(VW, S & B: 4.1-4.6)*

A. Definition of Work

We saw that *heat* is a way of changing the energy of a system by virtue of a temperature difference only.

Any other means for changing the energy of a system is called *work*. We can have push-pull work (*e.g.* in a piston-cylinder, lifting a weight), electric and magnetic work (*e.g.* an electric motor), chemical work, surface tension work, elastic work, *etc.*

In defining work, we focus on the effects that the system (*e.g.* an engine) has on its surroundings.   Thus we define work as being positive when the system does work on the surroundings (energy leaves the system). If work is done on the system (energy added to the system), the work is negative.

B. Consider a simple compressible substance

Work done by system

$$dW = \text{Force} \cdot dl$$

$$dW = \left(\frac{\text{Force}}{\text{Area}} \right)(\text{Area} \cdot dl)$$

$$dW = \text{Pressure} \cdot d\text{Volume}$$

$$dW = p_{ext}dV$$

therefore:
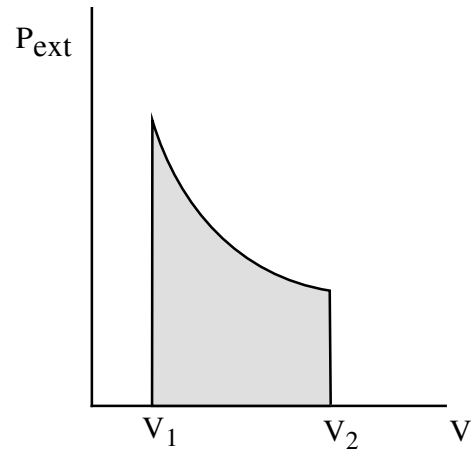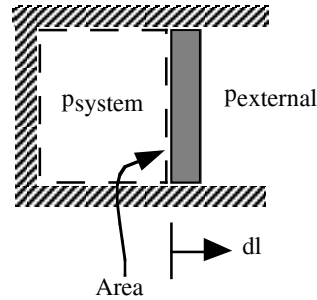
$$\boxed{W = \int_{V_1}^{V_2} p_{ext}dV}$$

or in terms of the specific volume, v:

$$\boxed{W = m\int_{v_1}^{v_2} p_{ext}dv}$$

where m is the mass of the system.

1. If system volume *expands* against a force, *work is done by the system*.

2. If system volume contracts under a force, work is done on the system.

3. Why $p_{external}$ instead of p_{system}?

> Consider $p_{external} = 0$ (vacuum). No work is done by the system even though p_{system} changes and the system volume changes.

C. Quasi-static processes

Use of p_{ext} instead of p_{sys} is often inconvenient because it is usually the state of the system that we are interested in.

However, for quasi-static processes $p_{sys} \approx p_{ext.}$

Consider $p_{ext} = p_{sys} \pm dp$

$$W = \int_{V_1}^{V_2} p_{ext}dV \qquad = \int_{V_1}^{V_2}\left(p_{sys} \pm dp\right)dV \qquad = \int_{V_1}^{V_2} p_{sys}dV \pm dpdV$$

therefore

$$W = \int_{V_1}^{V_2} p_{sys}dV$$

is the work done by the system in a quasi-static process.

1. Can only relate work to system pressure for quasi-static processes.

2. Take a free expansion ($p_{ext} = 0$) for example: p_{sys} is not related to p_{ext} (and thus the work) at all -- the system is not in equilibrium.

D. **Work is a path dependent process**

1. Work depends on path

2. Work is not a function of the state of a system

3. Must specify path if we need to determine work
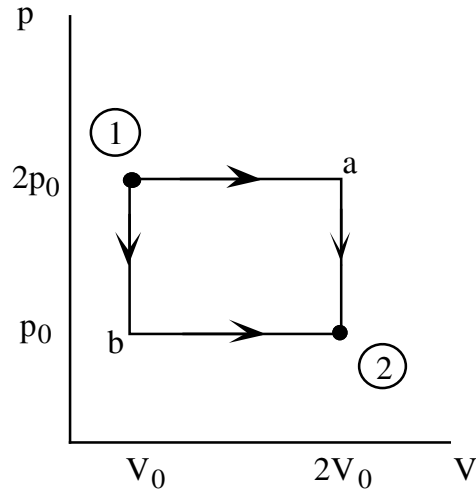
Along Path a: $W = 2p_0(2V_0 - V_0) = 2p_0V_0$

Along Path b: $W = p_0(2V_0 - V_0) = p_0V_0$

4. **Question:** Given a piston filled with air, ice, a bunsen burner, and a stack of small weights, describe how you would use these to move along either path a or path b above. When you move along either path how do you physically know the work is different?

5. Example: Work during quasi-static, isothermal expansion of a thermally perfect gas from p_1, V_1 to p_2, V_2.

First, is path specified? Yes -- isothermal.
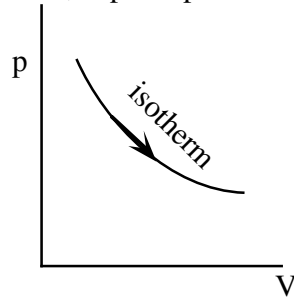
Equation of state for thermally perfect gas

$pV = n\mathcal{R}T$ n = number of moles
$\mathcal{R} =$ Universal gas constant
V = total system volume

$$W = \int_{V_1}^{V_2} \frac{n\mathcal{R}T}{V} dV \qquad = n\mathcal{R}T \int_{V_1}^{V_2} \frac{dV}{V} \qquad = n\mathcal{R}T \cdot \ln\left(\frac{V_2}{V_1}\right)$$

also for T = constant, $p_1 V_1 = p_2 V_2$, so the work done by the system is
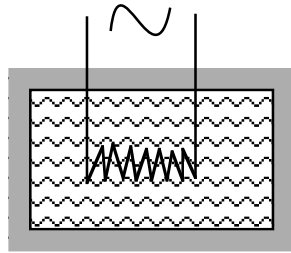
$$W = n\mathcal{R}T \cdot \ln\left(\frac{V_2}{V_1}\right) \qquad = n\mathcal{R}T \cdot \ln\left(\frac{p_1}{p_2}\right)$$

or in terms of the specific volume and the system mass

$$W = mRT \cdot \ln\left(\frac{v_2}{v_1}\right) \qquad = mRT \cdot \ln\left(\frac{p_1}{p_2}\right)$$

E. Work vs. heat transfer -- which is which?

1. Can have one, the other, or both. It depends on what crosses the system boundary. For example consider a resistor that is heating a volume of water.

2. If the water is the system, then the state of the system will be changed by heat transferred from the resistor.

3. If the system is the water + the resistor, then the state of the system will be changed by (electrical) work.

FIRST LAW OF THERMODYNAMICS: CONSERVATION OF ENERGY

I.   First Law of Thermodynamics *(VW, S & B: 2.6)*

A. <u>There exists for every system a property called energy</u>. **E = internal energy (arising from molecular motion - primarily a function of temperature) + kinetic energy + potential energy + chemical energy.**

1. Defines a useful property called "energy".

2. The two new terms in the equation (compared to what you have seen in physics and dynamics, for example) are the internal energy and the chemical energy. For most situtations in this class, we will neglect the chemical energy.

3. Let's focus on the internal energy, u. It is associated with the random or disorganized motion of the particles.

T_1 T_2

(molecular motion)   (molecular motion)
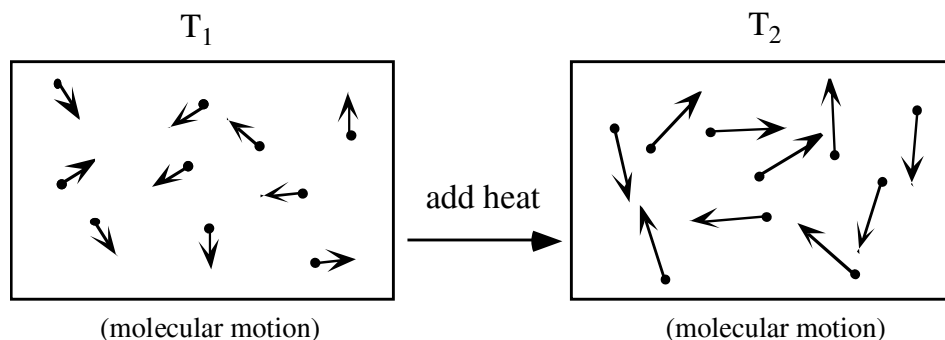
u is a function of the state of the system. Thus u = u (p, T), or u = u (p, v), or u = u(v,T). Recall that for pure substances the entire state of the system is specified if any <u>two</u> properties are specified. We will discuss the equations that relate the internal energy to these other variables later in the class.

B. The change in energy of a system is equal to the difference between the heat *added to* the system and the work *done by* the system. (This tells what the property energy is useful for.) *(VW, S & B: Chapter 5)*

$$\boxed{\Delta E = Q - W \qquad \text{(units are Joules)}}$$

1. The signs are important (and sometimes confusing!)

    E is the energy of the system
    Q is the heat transferred to the system (positive) - if it is transferred
    from the system Q is negative. *(VW, S & B: 4.7-4.8)*
    W is the work done by the system (positive) - if work is done on
    the system W is negative. *(VW, S & B: 4.1-4.4)*

2. The equation can also be written on a per unit mass basis

    $\Delta e = q - w$ (units are J/kg)

3. In many situations the potential energy and the kinetic energy of the system
    are constant.

    Then $\Delta e = \Delta u$, and

    $\Delta u = q - w$ or $\Delta U = Q - W$

    Q and W are path dependent, U is not it depends only on the state of the
    system, not how the system got to that state.

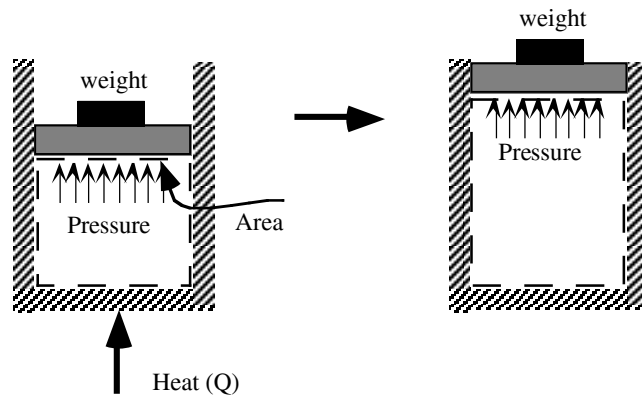4. Can also write the first law in differential form:

    $$\boxed{dU = \delta Q - \delta W \quad \text{or} \quad du = \delta q - \delta w}$$

    Here the symbol "δ" is used to denote that these are not exact differentials but
    are dependent on path.

5. Or for quasi-static processes

    $$\boxed{dU = \delta Q - pdV \qquad \text{or} \qquad du = \delta q - pdv}$$

6. Example: Heat a gas, it expands against a weight. Force (pressure times area)
   is applied over a distance, work is done.

7. We will see later that the First Law can be written for a control volume with steady mass flow in and steady mass flow out (like a jet engine for example). We will call this the Steady-Flow Energy Equation. *(VW, S & B: 5.8-5.12)*

8. We will spend most of the course dealing with various applications of the first law - in one form or another.

II.   Corollaries of the First Law

A. Work done in any adiabatic (Q=0) process is path independent.

$$\Delta U = \cancel{Q}^{0} - W$$
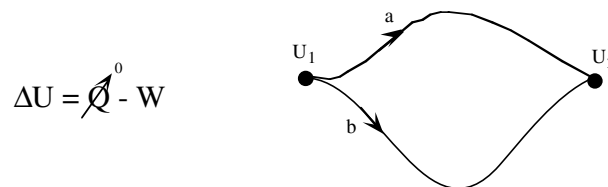
B. 2. For a cyclic process heat and work transfers are numerically equal
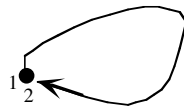
$U_{final} = U_{initial}$ therefore $\Delta U = 0$

and $Q = W$

or $\oint \delta Q = \oint \delta W$

III. Example applications of the First Law to motivate the use of a <u>property called "enthalpy"</u> *(VW, S & B: 5.4-5.5)*

A. The combination u+pv shows up frequently so we give it a name: "enthalpy" h= u+pv (or H = U+pV). It is a function of the state of the system.

The utility and physical significance of enthalpy will be clearer when we discuss the steady flow energy equation in a few lectures. For now, you may wish to think of it as follows (Levenspiel, 1996). When you evaluate the energy of an object of volume V, you have to remember that the object had to push the surroundings out of the way to make room for itself. With pressure p on the object, the work required to make a place for itself is pV. This is so with any object or system, and this work may not be negligible. (Recall, the force of one atmosphere pressure on one square meter is equivalent to the force of a mass of about 10 tons.) Thus the total energy of a body is its internal energy plus the extra energy it is credited with by having a volume V at pressure p. We call this total energy the enthalpy, H.
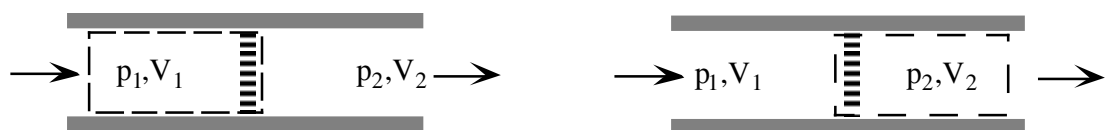
B. Consider a quasi-static process of constant pressure expansion

$$Q = (U_2 - U_1) + W$$
$$= (U_2 - U_1) + p(V_2 - V_1) \qquad \text{since } p_1 = p_2 = p$$

so $\qquad Q = (U_2 + pV_2) - (U_1 + pV_1) = H_2 - H_1$

C. Consider adiabatic throttling of a gas (gas passes through a flow resistance). What is the relation between conditions before and after the resistance?

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

or $\qquad U_2 - U_1 = -(p_2 V_2 - p_1 V_1)$

so $\qquad U_2 + p_2 V_2 = U_1 + p_1 V_1$

$H_2 = H_1$

IV. First Law in terms of enthalpy

$dU = \delta Q - \delta W$ (for any process, neglecting ΔKE and ΔPE)

$dU = \delta Q - pdV$ (for any quasi-static process, no ΔKE or ΔPE)

$H = U + pV$ therefore $dH = dU + pdV + Vdp$

so $dH = \delta Q - \delta W + pdV + Vdp$ (any process)

or

$$\boxed{dH = \delta Q + Vdp \text{ (for any quasi-static process)}}$$

V. Specific Heats and Heat Capacity *(VW, S & B: 5.6)*

A. <u>Question</u>**: Throw an object from the top tier of the lecture hall to the front of the room. Estimate how much the temperature of the room has changed as a result. Start by listing what information you need to solve this problem.**

B. How much does a given amount of heat transfer change the temperature of a substance? It depends on the substance. In general

$$Q = C\Delta T$$

where C is a constant that depends on the substance.

1. For a constant pressure process

$$C_p = \left(\frac{\delta Q}{\partial T}\right)_p \qquad \text{or} \qquad c_p = \left(\frac{\delta q}{\partial T}\right)_p$$

and for a constant volume process

$$C_v = \left(\frac{\delta Q}{\partial T}\right)_v \qquad \text{or} \qquad c_v = \left(\frac{\delta q}{\partial T}\right)_v$$

we use c_p and c_v to relate u and h to the temperature for an ideal gas.

2. <u>Expressions for u and h.</u> Remember that if we specify any two properties of the system, then the state of the system is fully specified. In other words we can write $u = u(T,v)$, $u=u(p,v)$ or $u=u(p,T)$ -- the same holds true for h. *(VW, S & B: 5.7)*

Consider a constant volume process and write $u = u(T,v)$. Then

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

where the last term is zero since there is no change in volume. Now if we write the First Law for a quasi-static process

$$du = \delta q - pdv$$

where again the last term is zero since there is no volume change. So

$$\delta q = \left(\frac{\partial u}{\partial T}\right)_v dT \qquad so \qquad \left(\frac{\partial u}{\partial T}\right)_v = \left(\frac{\delta q}{\partial T}\right)_v = c_v$$

so

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v$$

If we write h=h(T,p), and consider a constant pressure process, we can perform similar manipulations and show that

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p$$

c_p and c_v are thermodynamic properties of a substance. The previous two relationships are <u>valid at any point in any quasi-static process</u> whether that process is constant volume, constant pressure, or neither.

C. Ideal gas assumption *(VW, S & B: 5.7)*

If we have a thermally perfect gas (i.e. it obeys pv=RT), then it is called an *ideal gas* if u = u(T) <u>only</u>, and h= h(T) <u>only</u>. Then

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \underset{0}{\left(\frac{\partial u}{\partial v}\right)_T} dv$$

and

$$dh = \left(\frac{\partial h}{\partial T}\right)_p dT + \underset{0}{\left(\frac{\partial h}{\partial p}\right)_T} dp$$

so for an ideal gas

$$\boxed{du = c_v dT \qquad and \qquad \Delta u_{1-2} = \int_{T_1}^{T_2} c_v(T)dT}$$

- 21 -

and

$$dh = c_p dT \qquad \text{and} \qquad \Delta h_{1-2} = \int_{T_1}^{T_2} c_p(T) dT$$

Over small temperature changes ($\Delta T \approx 200K$), it is often assumed that c_v and c_p are constant.

D. First Law Expressions for an Ideal Gas

1. For an ideal gas undergoing a quasi-static process:

$$\delta q = c_v dT + pdv$$

or in terms of enthalpy

$$\delta q = c_p dT - vdp$$

2. Relationships between thermodynamic properties c_v, c_p, and R

   a) Equating the two first law expressions given above

   $$c_p dT - vdp = c_v dT + pdv$$

   $$(c_p - c_v)dT = d(pv)$$

   $$c_p - c_v = d(pv)/dT \qquad \text{and } pv = RT$$

   so
   $$c_p - c_v = R$$

   b) The ratio of specific heats, γ

   $$\gamma = c_p/c_v$$

3. Example: Quasi-static, adiabatic process for an ideal gas

   $$\overset{0}{\cancel{\delta q}} = c_v dT + pdv \quad \text{and} \quad \overset{0}{\cancel{\delta q}} = c_p dT - vdp$$

   so
   $$c_v\, dT = -pdv \quad \text{and} \quad c_p\, dT = vdp$$

   therefore

   $$\frac{c_p}{c_v} = -\frac{v}{p}\frac{dp}{dv} \qquad \text{or} \qquad \gamma\frac{dv}{v} = -\frac{dp}{p}$$

   then

$$\gamma \ln \frac{v_2}{v_1} + \ln \frac{p_2}{p_1} = 0$$

or

$$\frac{p_2 v_2^{\gamma}}{p_1 v_1^{\gamma}} = 1$$

finally, we arrive at the very useful expression

$$pv^{\gamma} = \text{constant}$$

from which it can also be shown that

$$\frac{p_2}{p_1} = \left(\frac{T_2}{T_1}\right)^{\gamma/\gamma-1} \quad \text{and} \quad \frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{\gamma-1}$$

We will use the above equation to relate pressure and temperature to one another for quasi-static adiabatic processes (our idealization of what happens in compressors and turbines).

E. Questions:

1. On a p-v diagram for a closed-system sketch the thermodynamic paths that the system would follow if expanding from volume = v_1 to volume = v_2 by isothermal and quasi-static, adiabatic processes.

2. For which process is the most work done by the system?

3. For which process is there heat exchange?   Is it added or removed?

4. Is the final state of the system the same after each process?

5. Derive expressions for the work done by the system for each process.

APPLICATIONS OF THE FIRST LAW
TO HEAT ENGINES

I.   Thermodynamic cycles and heat engines *(VW, S & B: Chapter 9)*

This section of the course is devoted to describing the basic fundamentals of how various heat engines work (e.g. a refrigerator, an IC engine, a jet). You will also learn how to model these heat engines as thermodynamic cycles and how to apply the First Law of Thermodynamics to estimate thermal efficiency and work output as a function of pressures and temperatures at various points in the cycle. This is called **ideal cycle analysis**. The estimates you obtain from the analysis represent the best achievable performance that may be obtained from a heat engine. In reality, the performance of these systems will be somewhat less than the estimates obtained from ideal cycle analysis—you will learn how to make more realistic estimates in 16.050.

We will deal with only "air-standard" thermodynamic cycles, where we ignore the changes in properties of the working fluid brought about by the addition of fuel or the presence of combustion products (we do of course account for the heat release that occurs due to the combustion of the fuel-air mixture). In general this is a good assumption since in typical combustion applications the fuel accounts for only about 5% of the mass of the working fluid.

A. The Otto Cycle (VW, S & B: 9.13)

The Otto cycle is an idealization of a set of processes used by spark ignition internal combustion engines (2-stroke or 4-stroke cycles). These engines a) ingest a mixture of fuel and air, b) compress it, c) cause it to react, thus effectively adding heat through converting chemical energy into thermal energy, d) expand the combustion products, and then e) eject the combustion products and replace them with a new charge of fuel and air. The various steps are illustrated on page 9 of these notes. There is a nice animation (and other useful material) at http://www.uq.edu.au/~e4nsrdja/teaching/e4213/intro.htm

We model all of these happenings by a thermodynamic cycle consisting of a set of processes all acting on a fixed mass of air contained in a piston-cylinder arrangement. The exhaust and intake processes are replaced by constant-volume cooling.

1. Representation of the heat engine as a thermodynamic cycle.

   (Ingest mixture of fuel and air)

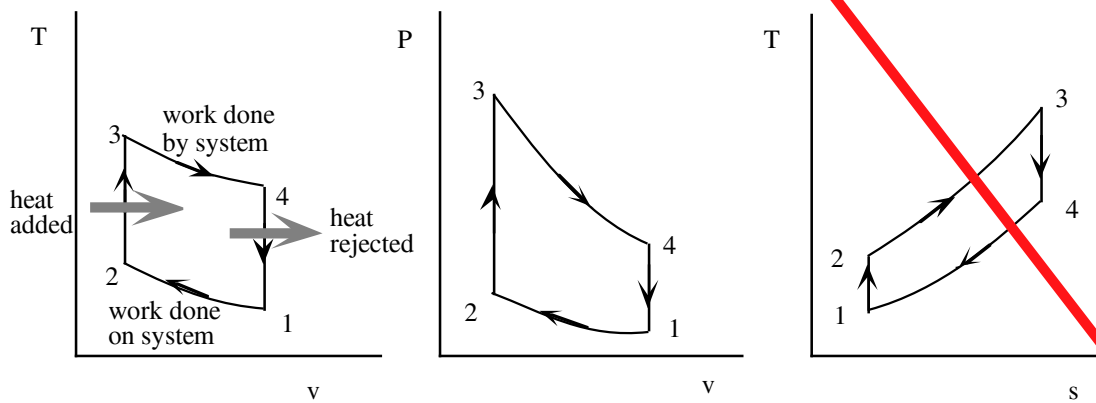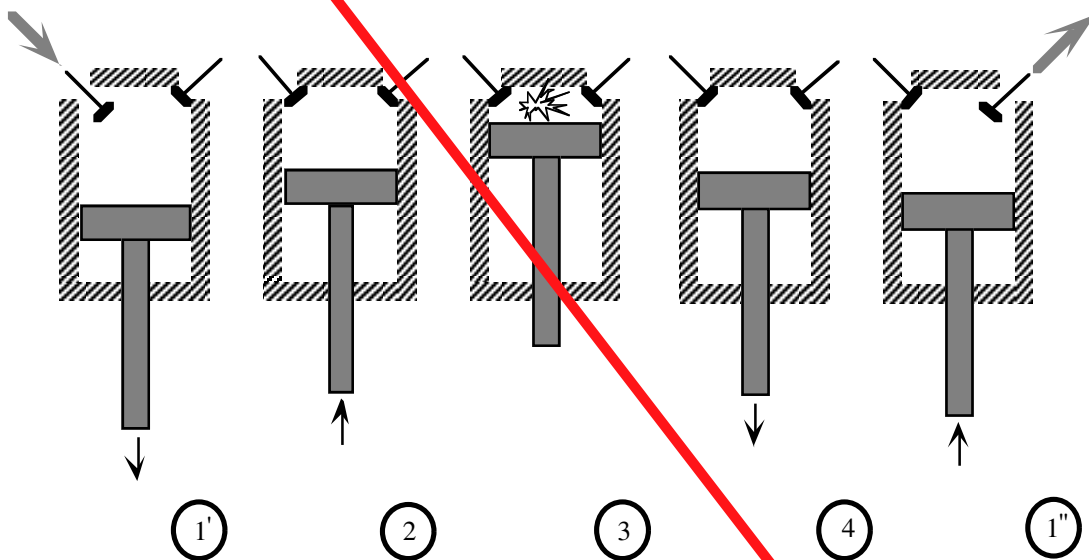   1' - 2 Compress mixture quasi-statically and adiabatically

   2 - 3 Ignite and burn mixture at constant volume (heat is added)

   3 - 4 Expand mixture quasi-statically and adiabatically

   4 - 1'' Cool mixture at constant volume

   (then repeat)

   work ~ Force* distance ~ $\int pdv$
   fuel use ~ heat added ~ $T_3 - T_2$
   efficiency ~ work out/fuel use

- 25 -

2. Method for estimating thermal efficiency and work output (application of the First Law of Thermodynamics).

a) **Net work done by system** = work of expansion + work of compression (-)

Both expansion and compression are adiabatic so

$\Delta w = (u_3 - u_4) - (u_2 - u_1)$

Assuming an ideal gas with constant c_v

$\Delta w = c_v[(T_3 - T_4) - (T_2 - T_1)]$

b) While the above expression is accurate, it is not all that useful. We would like to put the expression in terms of the typical design parameters: the compression ratio ($v_1/v_2 = v_4/v_3$), and the heat added during combustion ($q_{comb.} = c_v(T_3 - T_2)$).

For a quasi-static, adiabatic process,

$\dfrac{T_2}{T_1} = \left(\dfrac{v_1}{v_2}\right)^{\gamma-1} = \dfrac{T_3}{T_4}$ so we can write the net work as

$\Delta w = c_v T_1 \left(\dfrac{T_4}{T_1} - 1\right)\left(r^{\gamma-1} - 1\right)$ we also know that

$\dfrac{T_4}{T_1} = \left(\dfrac{T_4}{T_3}\right)\left(\dfrac{T_3}{T_2}\right)\left(\dfrac{T_2}{T_1}\right) = \dfrac{T_3}{T_2}$ since $\dfrac{T_2}{T_1} = \dfrac{T_3}{T_4}$ so

$\dfrac{T_4}{T_1} - 1 = \dfrac{T_3}{T_2} - 1 = \left(\dfrac{T_3 - T_2}{T_1}\right)\left(\dfrac{1}{r^{\gamma-1}}\right)$

and finally, the desired result in terms of typical design parameters:

$$\boxed{\Delta w = q_{comb.} \dfrac{\left(r^{\gamma-1} - 1\right)}{r^{\gamma-1}}}$$
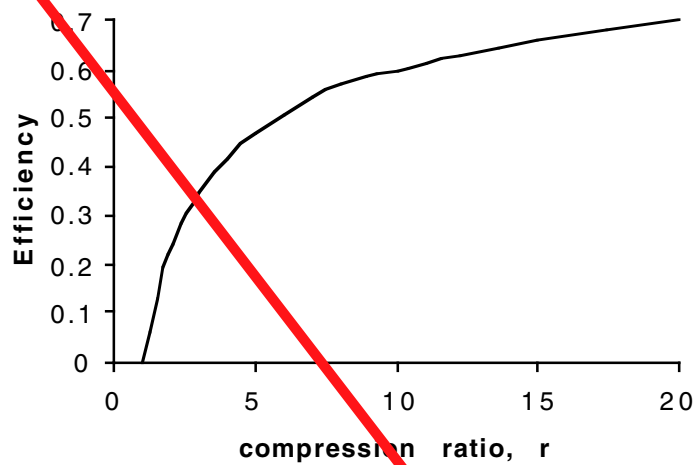
c) The **thermal efficiency** of the cycle is

$\eta = \dfrac{\text{net work}}{\text{heat input}} = \dfrac{\Delta w}{q_{comb.}}$ so

$$\eta_{Otto} = \frac{\left(r^{\gamma-1} - 1 \right)}{r^{\gamma-1}}$$

(Note that we could also rewrite this as:

$\eta_{Otto} = 1 - \frac{T_1}{T_2}$ showing that the efficiency of an Otto cycle depends only
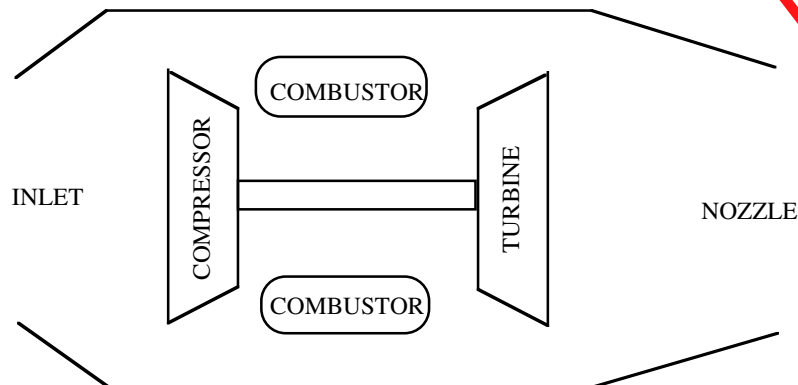
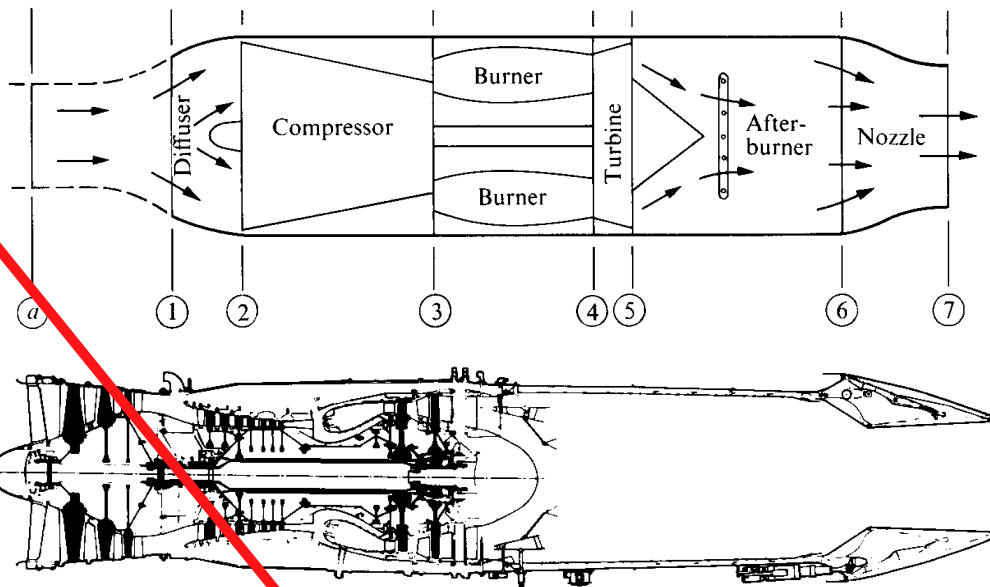on the temperature ratio of the compression process.)

Otto Cycle Efficiency

B. **Brayton Cycle (VW, S & B: 9.8-9.9, 9.12)**

The Brayton cycle is an idealization of a set of thermodynamic processes used in gas turbine engines, whether for jet propulsion or for generation of electrical power.

1. Components of a gas turbine engine

Schematics of typical military gas turbine engines. Top: turbojet with afterburning, bottom: GE F404 low bypass ratio turbofan with afterburning (Hill and Peterson, 1992).

2. The thermodynamic cycle

The cycle consists of four processes: a) quasi-static adiabatic compression in the inlet and compressor, b) constant pressure heat addition in the combustor, c) quasi-static adiabatic expansion in the turbine and exhaust nozzle, and finally d) constant pressure cooling to get the working fluid back to the initial condition.

1 - 2 Adiabatic, quasi-static compression in inlet and compressor

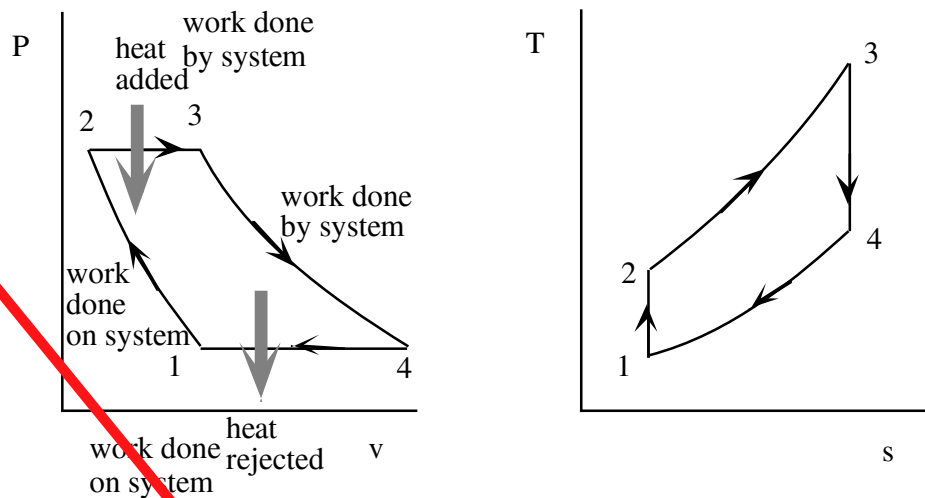2 - 3 Combust fuel at constant pressure (*i.e.* add heat)

3 - 4 Adiabatic, quasi-static expansion in turbine
        a. take work out and use it to drive the compressor
        b. take remaining work out and use it to accelerate fluid for jet
        propulsion, or to turn a generator for electrical power generation.

4 - 1 Cool the air at constant pressure

Then repeat

3. Estimating the performance of the engine

    Our objective with the Brayton cycle is the same as for the Otto cycle. First to
    derive expressions for the net work and the thermal efficiency of the cycle,
    and then to manipulate these expressions to put them in terms of typical
    design parameters so that they will be more useful.

    First, remember from the First Law we can show that <u>for any cyclic process
    heat and work transfers are numerically equal</u>

    $\Delta u = q - w$

    $u_{final} = u_{initial}$ therefore $\Delta u = 0$ and $q = w$ or $\oint \delta q = \oint \delta w$

    This fact is often useful for solving thermodynamic cycles. For instance in
    this example, we would like to find the net work of the cycle and we could
    calculate this by taking the difference of the work done all the way around the
    cycle. Or, since $\Delta q = \Delta w$, we could just as well consider the difference
    between the heat added to the cycle in process 2-3, and the heat rejected by
    the cycle in process 4-1.

    a) heat added between 2-3 (combustor):

        First Law in terms of enthalpy for an ideal gas undergoing a quasi-static
        process:
        $\delta q = dh - vdp$ or $\delta q = c_p dT - vdp$

        at constant pressure

        $q_{added} = c_p \Delta T$ or $q_{added} = c_p (T_3 - T_2)$

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b) heat rejected between 4-1:

similarly

$$q_{added} = c_p \, \Delta T \quad \text{or} \quad q_{rejected} = c_p \, (T_4 - T_1)$$

c) work done and thermal efficiency:

$$\Delta w = \Delta q = q_{added} - q_{rejected} = c_p[(T_3 - T_2) - (T_4 - T_1)]$$

$$\eta_{Brayton} = (q_{added} - q_{rejected})/ \, q_{added} = [(T_3 - T_2) - (T_4 - T_1)]/(T_3 - T_2)$$

Again, while these expressions are accurate, they are not all that useful. We need to manipulate them to put them in terms of typical design parameters for gas turbine engines. For gas turbine engines the most useful design parameters to use for these equations are often the inlet temperature (T_1), the <u>compressor pressure ratio</u> (p_2/p_1), and the maximum cycle temperature, the <u>turbine inlet temperature</u> (T_3).

d) Rewriting equations in terms of design parameters:

$$\Delta w = c_p T_1 \left(\frac{T_3}{T_1} - \frac{T_2}{T_1} - \frac{T_4}{T_1} + 1 \right)$$

$$\frac{p_2}{p_1} = \frac{p_3}{p_4} = \left(\frac{T_2}{T_1} \right)^{\gamma/\gamma-1} = \left(\frac{T_3}{T_4} \right)^{\gamma/\gamma-1} \quad \text{therefore} \quad \frac{T_2}{T_1} = \frac{T_3}{T_4} \quad \text{and} \quad \frac{T_4}{T_1} = \frac{T_3}{T_2}$$

so

$$\Delta w = c_p T_1 \left[\frac{T_3}{T_1} - \left(\frac{p_2}{p_1} \right)^{\gamma-1/\gamma} - \frac{T_3}{T_2} + 1 \right] \quad \text{with} \quad T_2 = T_1 \left(\frac{p_2}{p_1} \right)^{\gamma-1/\gamma}$$

becomes

$$\Delta w = c_p T_1 \left[\frac{T_3}{T_1} - \left(\frac{p_2}{p_1} \right)^{\gamma-1/\gamma} - \frac{T_3}{T_1} \left(\frac{p_2}{p_1} \right)^{-(\gamma-1)/\gamma} + 1 \right]$$
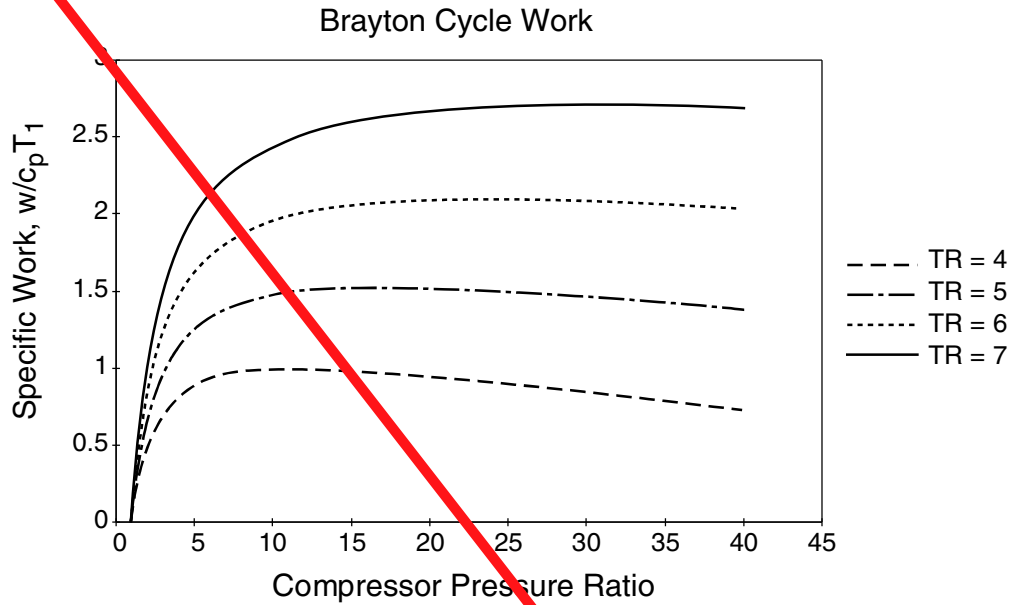
<u>and for the efficiency</u>

$$\eta = 1 - \left(\frac{T_4 - T_1}{T_3 - T_2} \right) \qquad = 1 - \frac{T_1}{T_2} \left[\frac{\dfrac{T_4}{T_1} - 1}{\dfrac{T_3}{T_2} - 1} \right] \qquad \text{but from above}$$
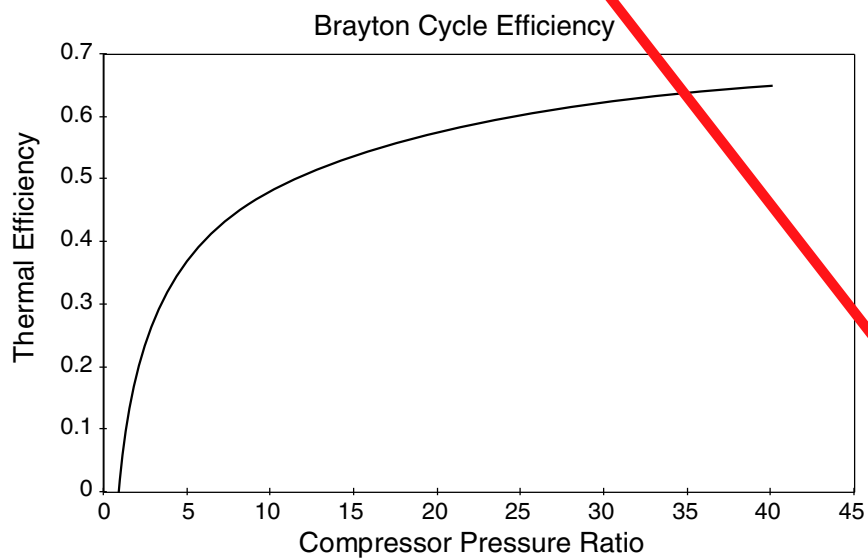
$$\frac{T_4}{T_1} = \frac{T_3}{T_2}$$

so

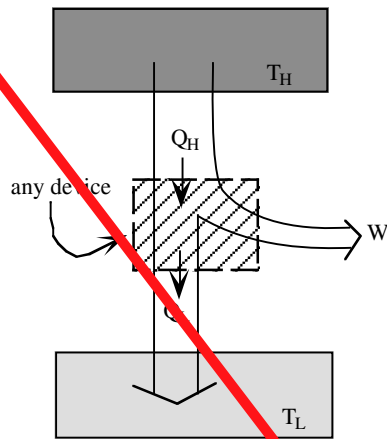$$\eta_{\text{Brayton}} = 1 - \frac{T_1}{T_2} = 1 - \frac{1}{\left(\dfrac{p_2}{p_1}\right)^{\gamma-1/\gamma}}$$

e) Performance plots

Brayton Cycle Work

In the plot above, TR = T_3/T_1. Note that for a given turbine inlet temperature, T_3, (which is set by material limits) there is a compressor pressure ratio that maximizes the work.

Brayton Cycle Efficiency

C. Generalized Representation of Thermodynamic Cycles *(VW, S & B: 6.1)*

Note that **heat engines** can be represented generally as:

a transfer of heat from a high temperature reservoir to a device
+
a rejection of heat from a device to a low temperature reservoir
+
net work done on surroundings

D. To obtain data for an operating gas turbine engine (the one that provides power to MIT!) checkout the following links: http://cogen.mit.edu/index.htm and http://cogen.mit.edu/unified/
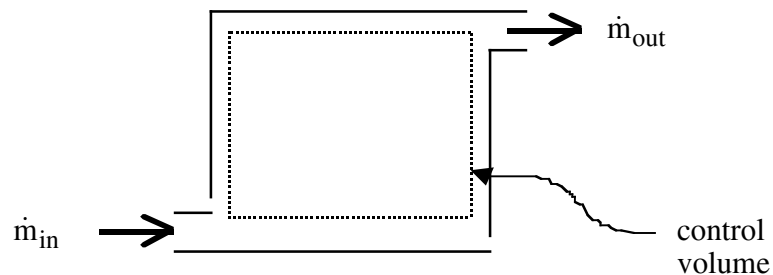
STEADY FLOW ENERGY EQUATION

I.   First Law for a Control Volume (VW, S & B: Chapter 6)

A. Frequently (especially for flow processes) it is most useful to express the First Law as a statement about <u>rates</u> of heat and work, for a control volume.

1.   Conservation of mass *(VW, S & B: 6.1)*

$$\frac{dm_{cv}}{dt} = \dot{m}_{in} - \dot{m}_{out} \qquad \begin{pmatrix} \text{rate of change} \\ \text{of mass in c.v.} \end{pmatrix} = \begin{pmatrix} \text{mass flow} \\ \text{in} \end{pmatrix} - \begin{pmatrix} \text{mass flow} \\ \text{out} \end{pmatrix}$$

For steady state, $\dfrac{d}{dt} = 0$ therefore

$$\dot{m}_{in} = \dot{m}_{out} = \dot{m}$$

2.   Conservation of Energy (First Law) *(VW, S & B: 6.2)*

Recall, $dE = \delta Q - \delta W$

For the control volume,

$$\frac{dE_{c.v.}}{dt} = \dot{Q}_{c.v.} - \dot{W}_{c.v.} + \dot{m}_{in}e_{in} - \dot{m}_{out}e_{out}$$

$$\left(\begin{matrix}\text{rate of change}\\ \text{of energy in c.v.}\end{matrix}\right) = \left(\begin{matrix}\text{rate of heat}\\ \text{added to c.v.}\end{matrix}\right) - \left(\begin{matrix}\text{rate of work}\\ \text{done}\end{matrix}\right) + \left(\begin{matrix}\text{rate of energy}\\ \text{flow in to c.v.}\end{matrix}\right) - \left(\begin{matrix}\text{rate of energy}\\ \text{flow out of c.v.}\end{matrix}\right)$$

where

$$\dot{Q} = \lim_{dt \to 0}\left(\frac{\delta Q}{dt}\right) \quad \text{rate of energy transfer to the system as heat}$$

$$\dot{W} = \lim_{dt \to 0}\left(\frac{\delta W}{dt}\right) \quad \text{rate of work done by the system}$$

3. For steady-state *(VW, S & B: 6.3)*

$$\frac{d}{dt} = 0 \quad \text{and} \quad \dot{m}_{in} = \dot{m}_{out} = \dot{m}$$

so

$$\dot{Q}_{c.v.} - \dot{W}_{c.v.} = \dot{m}(e_{out} - e_{in}) \qquad \text{(units J/s)}$$

or

$$\dot{Q}_{c.v.} - \dot{W}_{c.v.} = \dot{m}\left[(IE + KE + PE + CE)_{out} - (IE + KE + PE + CE)_{in}\right]$$

Neglecting potential and chemical energy (PE and CE)

$$\dot{Q}_{c.v.} - \dot{W}_{c.v.} = \dot{m}\left[\left(u + \frac{c^2}{2}\right)_{out} - \left(u + \frac{c^2}{2}\right)_{in}\right]$$

Where c is the speed of the fluid, and $c^2/2$ is the kinetic energy of the fluid per unit mass relative to some coordinate system.

If we divide through by the mass flow and set the inlet of the control volume as station 1, and the outlet as station 2, then

$$q_{1-2} - w_{1-2} = u_2 - u_1 + \frac{c_2{}^2}{2} - \frac{c_1{}^2}{2}$$

It is also more convenient to divide the work into two terms: 1) the <u>flow work</u> done by the system which is $p_2v_2 - p_1v_1$, and 2) any additional work which we will term <u>external work or shaft work</u>, w_s. Then we have

$$q_{1-2} - w_{s1-2} = \left(u_2 + p_2 v_2\right) - \left(u_1 + p_1 v_1\right) + \frac{c_2^2}{2} - \frac{c_1^2}{2}$$

or

$$\boxed{q_{1-2} - w_{s1-2} = h_2 - h_1 + \frac{c_2^2}{2} - \frac{c_1^2}{2}}$$

We will call this the **steady flow energy equation.**

For an **ideal gas** $dh = c_p dT$ so

$$q_{1-2} - w_{s1-2} = \left(c_p T_2 + \frac{c_2^2}{2}\right) - \left(c_p T_1 + \frac{c_1^2}{2}\right)$$

4. Flow work and shaft work

Enthalpy is most useful for separating flow work from shaft work. In the figure shown below. Heat is added, a compressor is doing work on the system, the flow entering the system does work on the system (work = $-p_1 V_1$), and work is done by the system through pushing out the flow (work = $+p_2 V_2$). The first law relates the change in energy between states 1 and 2 to the difference between the heat added and the work done by the system. Frequently, however, we are interested only in the shaft work that crosses the system boundary, not the volumetric or flow work. In this case it is most convenient to work with enthalpy.
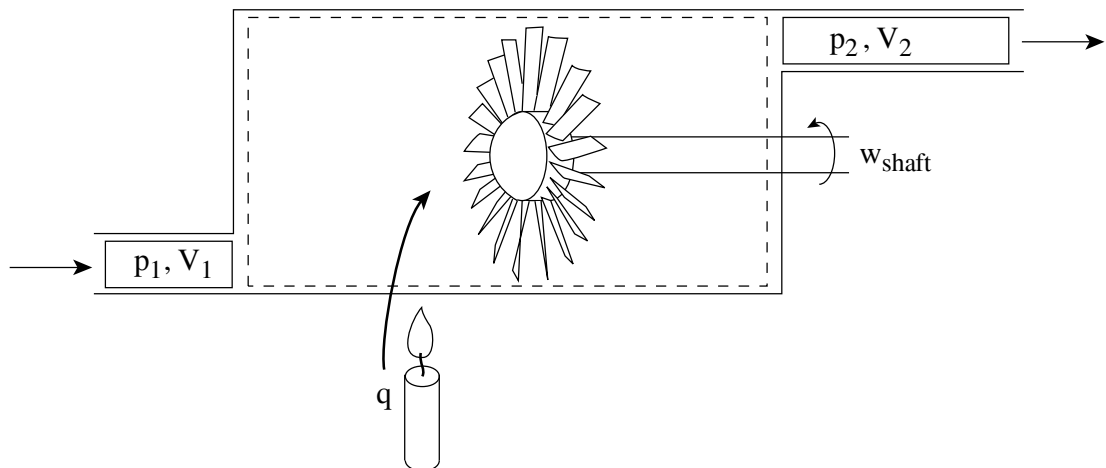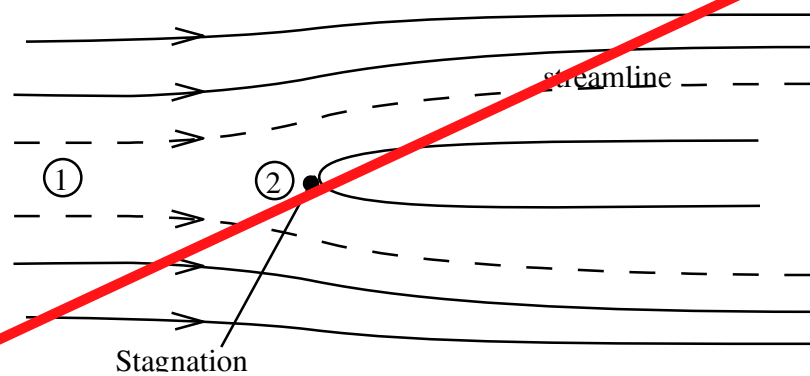

Note that both of the following cases are also frequently encountered:
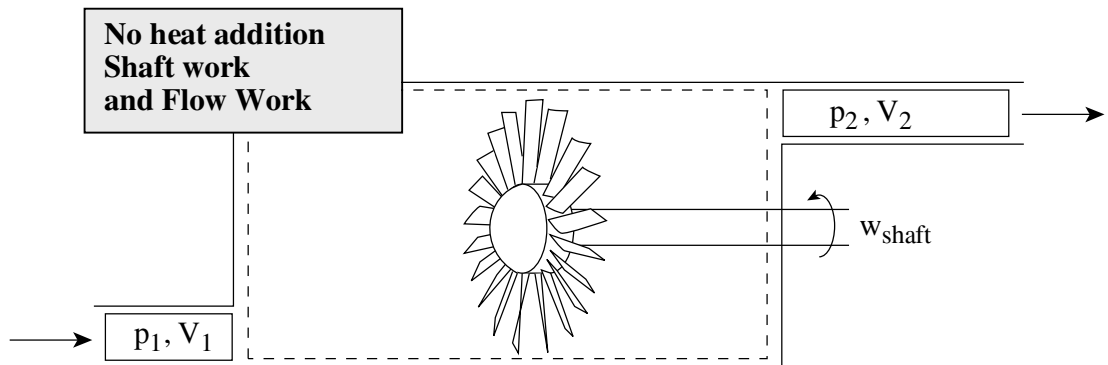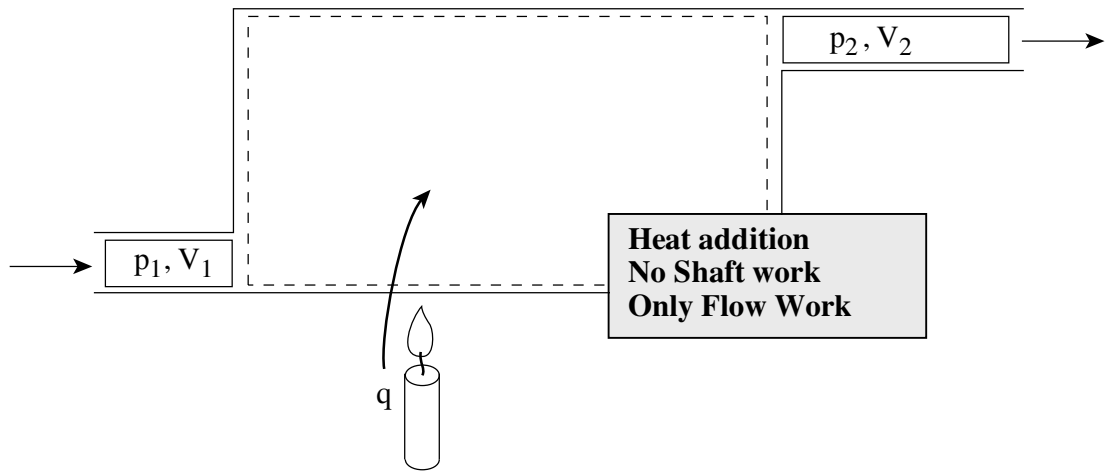
B. Stagnation Temperature and Stagnation Enthalpy

Suppose that our steady flow control volume is a set of streamlines describing the flow up to the nose of a blunt object.

The streamlines are stationary in space, so there is no external work done on the fluid as it flows. If there is also no heat transferred to the flow (adiabatic), then the steady flow energy equation becomes

$$c_p T_2 + \frac{c_2{}^2}{2} = c_p T_1 + \frac{c_1{}^2}{2}$$

1. The quantity that is conserved is called the stagnation temperature.

$$T_T = T + \frac{c^2}{2c_p} \qquad \left(\text{or} \quad \frac{T_T}{T} = 1 + \frac{\gamma - 1}{2} M^2 \qquad \text{using } a = \sqrt{\gamma RT} \right)$$

The stagnation temperature is the temperature that the fluid would reach if it were brought to zero speed by a steady adiabatic process with no external work. Note that for any steady, adiabatic flow with no external work, the stagnation temperature is constant.

(The Mach number, M, is the ratio of the flow speed, c, to the speed of sound, a. You will learn more about these quantities in fluids, but it is interesting to see that M^2 measures the ratio of the kinetic energy of the gas to its thermal energy.)

2. It is also convenient to define the **stagnation enthalpy**, h_T

$$\boxed{h_T = c_p T + \frac{c^2}{2}}$$

So we can write the **Steady Flow Energy Equation** in a convenient form as

$$\boxed{q_{1-2} - w_{s1-2} = h_{T2} - h_{T1}}$$

3. Note that for a quasi-static adiabatic process

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2} \right)^{\frac{\gamma - 1}{\gamma}} \qquad \text{so we can write} \qquad \frac{T_T}{T} = \left(\frac{p_T}{p} \right)^{\frac{\gamma - 1}{\gamma}}$$

and define the relationship between **stagnation pressure** and **static pressure** as

$$\frac{p_T}{p} = \left(1 + \frac{\gamma - 1}{2}M^2\right)^{\gamma/\gamma-1}$$

where, the stagnation pressure is the pressure that the fluid would reach if it were brought to zero speed, via a steady, adiabatic, quasi-static process with no external work.

4.   Frame dependence of stagnation quantities

An area of common confusion is the frame dependence of stagnation quantities. The stagnation temperature and stagnation pressure are the conditions the fluid would reach <u>if</u> it were brought to zero speed *relative to some reference frame*, via a steady adiabatic process with no external work (add quasi-static for stagnation pressure).

What if the body or reference frame is moving? We know from looking at re-entry vehicles, that the skin temperature is much hotter than the atmospheric temperature. If the atmosphere is assumed still, and we stagnate a fluid particle on the nose of a high speed vehicle (carrying it along with the vehicle and thus essentially giving it kinetic energy) its stagnation temperature is given by

$$T_T = T + \frac{c^2}{2c_p}$$

where c is the vehicle speed. The temperature the skin reaches (to first approximation) is the stagnation temperature. The atmospheric temperature, T, is not frame dependent.

The confusion comes about because T is usually referred to as the **static** temperature and in common language this has a similar meaning as "stagnation". In fluid mechanics and thermodynamics *static* is commonly used to label the <u>thermodynamic properties</u> of the gas p, T, etc.—these are not frame dependent. *Stagnation* quantities are those the flow <u>would arrive at if</u> brought to zero speed relative to some reference frame, via a steady adiabatic process with no external work (add quasi-static for stagnation pressure). Stagnation quantities depend on the frame of reference.

Thus for a re-entry vehicle, the stagnation temperature (vehicle frame) is hotter than the atmospheric (static) temperature. And in a still atmosphere, the static temperature is the same as the stagnation temperature (atmospheric frame).

5.   Example:

For the case shown below, a jet engine is sitting motionless on the ground prior to take-off. Air is entrained into the engine by the compressor. The inlet can be assumed to be frictionless and adiabatic.

Atmosphere:
T_{atm}
p_{atm}
$M = 0$

Inlet ① 1

$M = 0.5$

Compressor

Exhaust jet,
$M = 0.8$
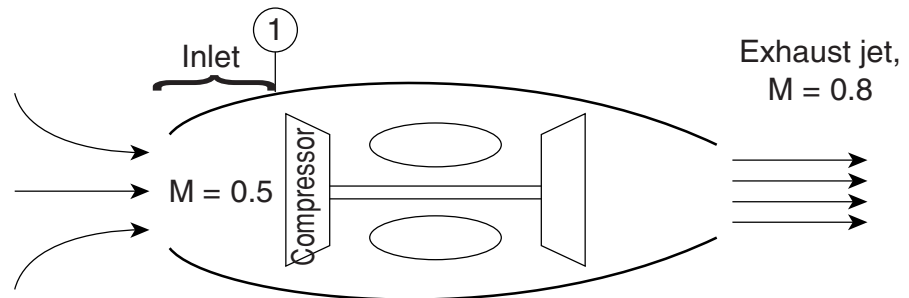
Considering the state of the gas within the inlet, prior to passage into the compressor, as state (1), and working in the *reference frame of the motionless airplane*:

a) Is T_{T1} greater than, less than, or equal to T_{atm}?

The stagnation temperature of the atmosphere, T_{Tatm}, is equal to T_{atm} since it is moving the same speed as the reference frame (the motionless airplane). The steady flow energy equation tells us that if there is no heat or shaft work (the case for our adiabatic inlet) the stagnation enthalpy (and thus stagnation temperature for constant Cp) remains unchanged. Thus $T_{T1} = T_{Tatm} = T_{atm}$

b) Is T_1 greater than, less than, or equal to T_{atm}?

If $T_{T1} = T_{atm}$ then $T_1 < T_{atm}$ since the flow is moving at station 1 and therefore some of the total energy is composed of kinetic energy (at the expense of internal energy, thus lowering T_1)

c) Is p_{T1} greater than, less than, or equal to p_{atm}?

Equal, by the same argument as a).

d) Is p_1 greater than, less than, or equal to p_{atm}?

Less than, by the same argument as b).

C. Example Applications of the Steady Flow Energy Equation *(VW, S & B: 6.4)*

1. Flow through a rocket nozzle

   A liquid bi-propellant rocket consists of a thrust chamber and nozzle and some means for forcing the liquid propellants into the chamber were they react, converting chemical energy to thermal energy.

fuel

combustion
chamber
c_c

oxidizer

c_e

hot, high pressure
low velocity gas
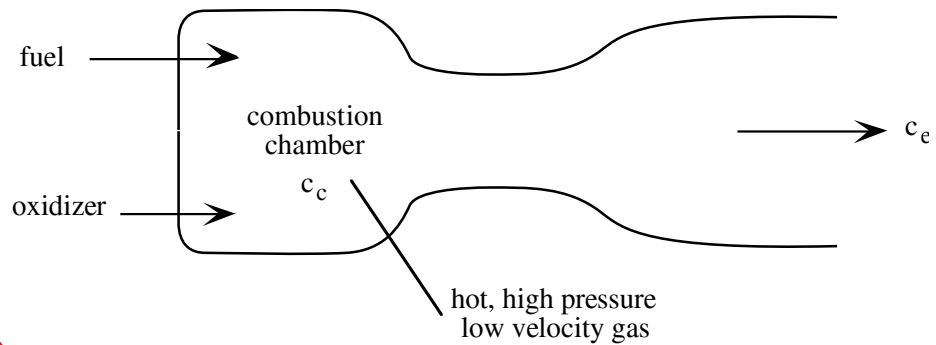
Once the rocket is operating we can assume that all of the flow processes are steady, so it is appropriate to use the steady flow energy equation. Also, for now we will assume that the gas behaves as an ideal gas, though in general this is a poor approximation. There is no external work, and we assume that the flow is adiabatic.

Then we can write the First Law as

$$q_{1-2} - w_{s1-2} = h_{T2} - h_{T1} \quad \text{which becomes} \quad h_{T2} = h_{T1}$$

or

$$c_p T_c + \frac{c_c^2}{2} = c_p T_e + \frac{c_e^2}{2}$$

therefore

$$c_e = \sqrt{2c_p(T_c - T_e)}$$

If we assume quasi-static, adiabatic expansion then

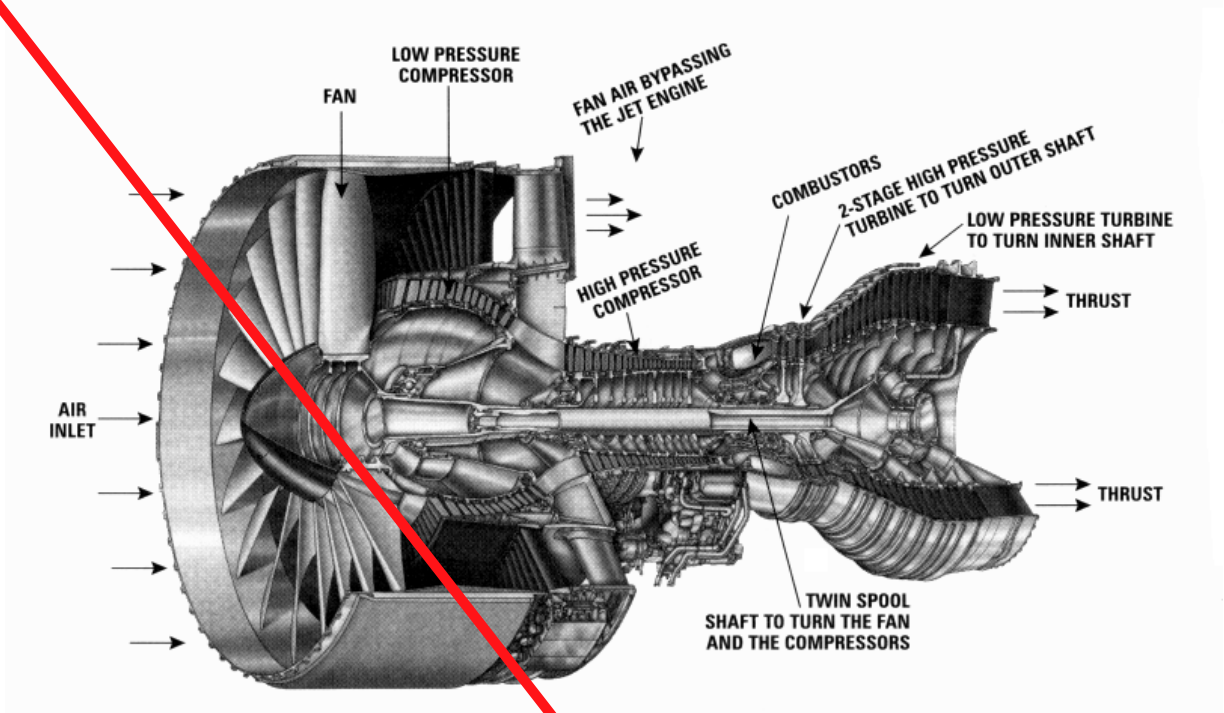$$\frac{T_e}{T_c} = \left(\frac{p_e}{p_c}\right)^{\frac{\gamma-1}{\gamma}} \quad \text{so}$$

$$c_e = \sqrt{2c_p T_c \left[1 - \left(\frac{p_e}{p_c}\right)^{\frac{\gamma-1}{\gamma}}\right]}$$

Where T_c and p_c are conditions in the combustion chamber (set by propellants), and p_e is the external static pressure.

2. Power to drive a gas turbine compressor

   Consider for example the PW4084 pictured below. The engine is designed to
   produce about 84,000 lbs of thrust at takeoff.

   The engine is a two-spool design. The fan and low pressure compressor are
   driven by the low pressure turbine. The high pressure compressor is driven by
   the high pressure turbine.

   π_f = total pressure ratio across the fan ≈ 1.4

   π_c = total pressure ratio across the fan + compressor ≈ 45

   $\dot{m}_f = 610 \text{ kg/s}$ $\qquad \dot{m}_{core} = 120 \text{ kg/s}$

   $T_{inlet} = 300\text{K}$

   Heat transfer from the gas streams is negligible so we write the First Law
   (steady flow energy equation) as:

   $$\overset{0}{\cancel{\dot{Q}}} - \dot{W}_s = \dot{m}(h_{T2} - h_{T1})$$

   For this problem we must consider two streams, the fan stream and the core
   stream, so

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$$-\dot{W}_s = \dot{m}_f \Delta h_{Tf} + \dot{m}_c \Delta h_{Tc}$$

$$= \dot{m}_f c_p \Delta T_{Tf} + \dot{m}_c c_p \Delta T_{Tc}$$

We obtain the temperature change by assuming that the compression process is quasi-static and adiabatic. So

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}$$

then $\quad \left(\dfrac{T_{T_2}}{T_{T_1}}\right)_{fan} = \left(\pi_f\right)^{\frac{\gamma-1}{\gamma}} = 1.1 \qquad \Rightarrow \Delta T_{T_{fan}} = 30K$

$$\left(\frac{T_{T_2}}{T_{T_1}}\right)_{core} = \left(\pi_{core}\right)^{\frac{\gamma-1}{\gamma}} = 3.0 \quad \Rightarrow \Delta T_{T_{core}} = 600K$$

$$-\dot{W}_s = 610\frac{kg}{s}\cdot 30K \cdot 1008\frac{J}{kg\ K} + 120\frac{kg}{s}\cdot 600K\cdot 1008\frac{J}{kg\ K}$$

$$= 91 \times 10^6 \text{ Joules/sec}$$

$$\dot{W}_s = -91 \text{ Megawatts} \qquad \begin{pmatrix}\text{negative sign implies} \\ \text{work done on the fluid}\end{pmatrix}$$

Note that 1 Hp = 745 watts

If a car engine ≈ 110Hp $= 8.2 \times 10^4$ watts,
then the power needed to drive compressor is equivalent to <u>1110</u> automobile engines.

All of this power is generated by the low pressure and high pressure turbines.

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REVERSIBLE AND IRREVERSIBLE PROCESSES, ENTROPY AND INTRODUCTION TO THE SECOND LAW

- So far we have dealt largely with ideal situations involving frictionless pistons and quasi-static pressure changes. We will now consider more general situations, and introduce the concept of entropy.

I. Irreversible Processes *(VW, S & B: 6.3-6.4)*

A. Consider a system composed of many bricks

thermal insulation

half at T_H hot (high)
half at T_L low
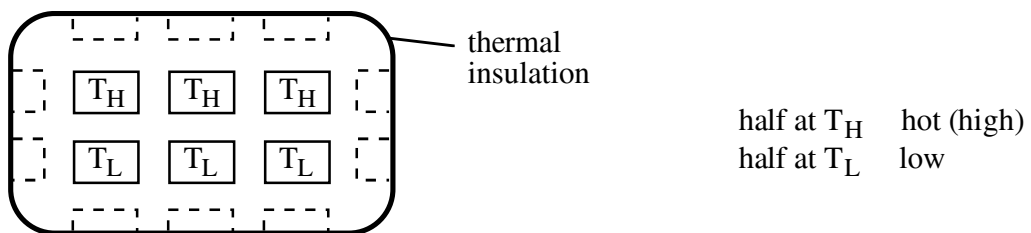
With these, we have the ability to obtain work by running a cycle between T_L and T_H.

What happens if put two bricks together? Applying the First Law:

$$cT_H + cT_L = 2cT_M$$

c = heat capacity = $\Delta Q/\Delta T$

for a solid

$$\left(\frac{\delta Q}{\partial T}\right)_p \approx \left(\frac{\delta Q}{\partial T}\right)_v$$

therefore

$$T_M = \frac{T_H + T_L}{2}$$

We have lost the ability to get work out of these two bricks. Can we restore the situation:

        a) without contact with outside?   - No.
        b) with contact from outside?   - Yes, but we have to do work.

Overall process:

> system is changed
> outside (rest of universe) is unchanged

Composite: system + rest of universe is changed by putting bricks together. The process is not **reversible**; That is there is no way to undo the change and leave no mark on the rest of the universe.

How do we measure this change?

1) Decreased ability to do work.
2) Energy? (This is conserved)

Measurement and characterization of this change is the subject of the Second Law of Thermodynamics. We will talk about this more later. For now let's look at another example.

B. Free vs. Reversible Expansions

What is the difference between a free expansion of a gas and an isothermal expansion against a piston? To answer this we examine what we would have to do to reverse, *i.e.* to undo, the process.

1. Free expansion

thermally insulated
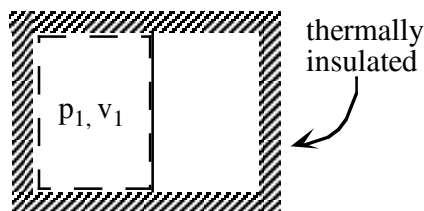
Remove the partition and $v_1 \rightarrow v_2$
The process is adiabatic (q = 0), and w = 0 since there is no motion of boundaries.
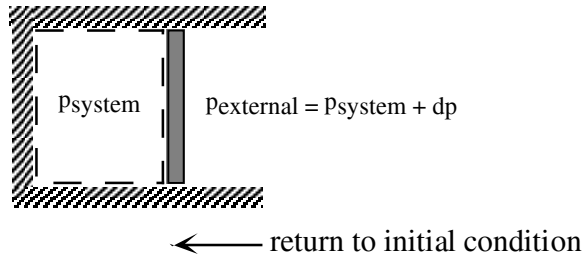
Therefore
$\Delta u = 0$

For an ideal gas $u = u(T) \Rightarrow T = \text{constant} = T_1$

State 1: v_1, T_1
State 2: v_2, T_1
$q = w = 0 \Rightarrow$ no change in surroundings

To restore the system to the original state $v_2 \rightarrow v_1$ at constant T, we compress isothermally by some external agency. We do this quasi-statically.

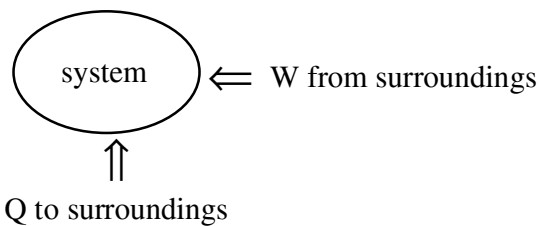During the return process:

$$\text{work} = \int p\,dv$$
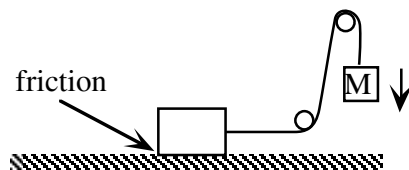
$$w = RT\ln\frac{v_2}{v_1} \quad \text{done } \underline{\text{on}} \text{ system}$$

$$q = RT\ln\frac{v_2}{v_1} \quad \text{rejected}$$

Q to surroundings

At end of the process:
   a) system is back in initial state (no change)
   b) surroundings (us) gave up work, w
   c) surroundings received heat, q

Sum of all these processes is that we converted work, w, to heat, q.

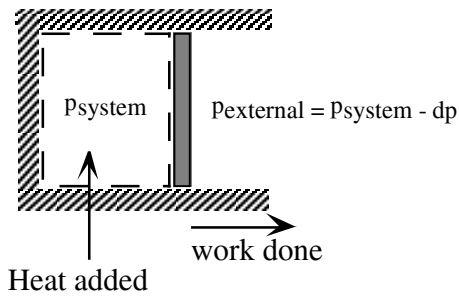Same as if let weight fall and pull block along rough surface 100% W → Q.

<u>Net effect</u>: system same + surroundings changed = universe has changed.

The process is not reversible.

2. Reversible expansion

Now consider an isothermal expansion against an external pressure which is

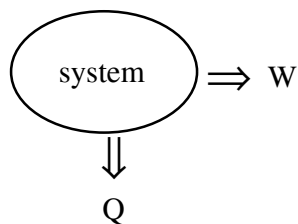only dp less that the pressure in the system.

During expansion, the work done on the surroundings is

$$\text{work} = \int p\, dv$$

$$w = RT \ln \frac{v_2}{v_1} \quad \text{done by system}$$

$$q = RT \ln \frac{v_2}{v_1} \quad \text{added to system}$$

Process during expansion

At the end of the isothermal expansion:
    a) surroundings have received work
    b) surroundings have given up heat

To restore the system to the original condition, we could put work back into system and reject heat to surroundings via a quasi-static isothermal compression just as we did following the free expansion.

Net result: system and surroundings back to initial state

The process is reversible.

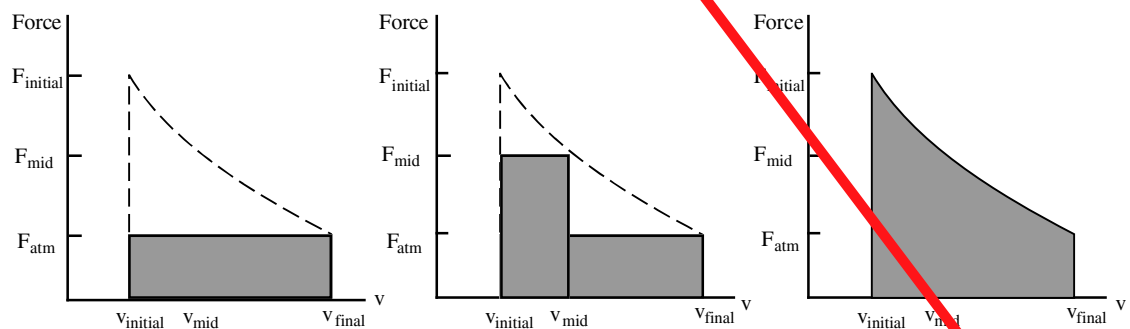## C. Reversibility, Irreversibility, and Lost Opportunity to Do Work

Maximum work is achieved during a reversible expansion (or compression).

For example, suppose we have a thermally insulated cylinder that holds an ideal gas. The gas is contained by a thermally insulated massless piston with a stack of many small weights on top of it. Initially the system is in mechanical and thermal equilibrium.
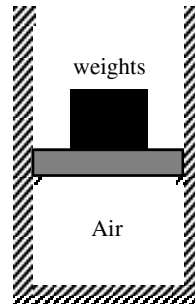
Consider the following three processes:

1) All of the weights are removed from the piston instantaneously and the gas expands until its volume is increased by a factor of four (a free expansion).

2) Half of the weight is removed from the piston instantaneously, the system is allowed to double in volume, and then the remaining half of the weight is instantaneously removed from the piston and the gas is allowed to expand until its volume is again doubled.

3) Each small weight is removed from the piston one at a time, so that the pressure inside the cylinder is always in equilibrium with the weight on top of the piston. When the last weight is removed, the volume has increased by a factor of four.

Maximum work (proportional to the area under these curves) is obtained for the quasi-static expansion. ***Note that there is a direct inverse relationship between the amount of work received from a process and the degree of irreversibility.**

II. Entropy as a Measure of Irreversibility *(VW, S & B: 6.5-6.6, 7.1)*

A. For a reversible (quasi-static), adiabatic process we can write the First Law as

$$du = \delta q - pdv$$

or

$$c_v dT = -pdv = -\frac{RT}{v}dv$$

thus

$$c_v \frac{dT}{T} = -R\frac{dv}{v}$$

We can think of the above equation as giving the <u>fractional change in temperature</u> in terms of the <u>fractional change of volume</u> for a reversible process. For instance, when the volume increases the temperature decreases; the consequent reduction in thermal energy is equivalent to the work done on the surroundings. The quantities c_v and R are scale factors for these two effects.

B. For an irreversible case

The volume increases with a smaller relative change in temperature and less work done on the surroundings. Recall the case of an adiabatic free expansion -- the temperature does not change at all, no work is done, but the volume increases.

We now introduce a property called **entropy**, and give it the symbol "**s**". We will use entropy change as a measure of how reversible a process is

$$ds = c_v \frac{dT}{T} + R\frac{dv}{v}$$

Note that if the volume increases without a proportionate decrease in temperature, then s increases.

C. Entropy as a State Variable *(VW, S & B: 7.10)*

Since T and v are state variables, it follows from the above equation that s is as well. For the case of a <u>thermally perfect gas</u> then

$$s - s_0 = \int_{T_0}^{T} c_v \frac{dT}{T} + R\ln\left(\frac{v}{v_0}\right)$$

or in situations with <u>c_v = constant</u>

$$s - s_0 = c_v \ln\left(\frac{T}{T_0}\right) + R \ln\left(\frac{v}{v_0}\right)$$

Also, writing

$$pv = RT \qquad \text{as} \qquad \frac{dv}{v} = \frac{dT}{T} - \frac{dp}{p}$$

we can get a relation for s(T,p) as well

$$ds = c_v \frac{dT}{T} + R\left(\frac{dT}{T} - \frac{dp}{p}\right) = c_p \frac{dT}{T} - R \frac{dp}{p}$$

So for the case of a <u>thermally perfect gas</u> then

$$s - s_0 = \int_{T_0}^{T} c_p \frac{dT}{T} - R \ln\left(\frac{p}{p_0}\right)$$

or in situations with <u>c_p = constant</u>

$$s - s_0 = c_p \ln\left(\frac{T}{T_0}\right) - R \ln\left(\frac{p}{p_0}\right)$$

III. Second Law of Thermodynamics *(VW, S & B: Chapter 6)*

A. <u>There exists for every system in equilibrium a property called entropy, s. (As with the Oth and 1st Laws, the 2nd Law starts by defining a useful property, "entropy".)</u>

Entropy is a function of the state of the system and can be found if any two properties of the system are known, *e.g.* s = s(p,T) or s = s (T,v) or s = s(p,v). We will discuss the equations that relate entropy to these other variables later in the class. *(VW, S & B: 7.2-7.4)*

B. **The total entropy change (system + surroundings) is always greater than or equal to zero for any change of state of the system.**

1. This is a statement that describes a useful behavior of this property "entropy". It turns out that the *most efficient processes possible* for converting energy from one form to another, are processes where the net entropy change of the system *and the* surroundings is zero. These processes represent limits - the best that can be done. In thermodynamics, propulsion, and power generation systems we often compare performance to these limits to measure how close to ideal a given process is.

2. *Physically*: Natural processes tend to go in certain directions, *e.g.* it is easier to mix two gases than to unmix them, and it is easier to bring two bricks initially at different temperatures to the same temperature than *vice versa*. Either direction satisfies the First Law. Second Law tells about the natural direction of processes and more importantly what the direction implies about the ability to do work with a system. *(VW, S & B: 6.3-6.4)*

   a) For example, consider an unrestrained expansion. We start with a thermally insulated (adiabatic) volume with a thin diaphragm in the middle. On one side of the diaphragm is vacuum, on the other is gas at some pressure. We open a hole in the diaphragm and the gas rushes through it. No work is done on surroundings, and there is no heat transfer, therefore there is no change in the energy of system (1st Law).
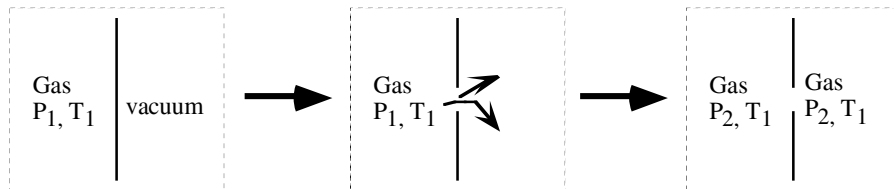
   b) Do we ever see the reverse happen? (Only if we somehow devised a process where the surroundings supplied some work.)

   c) The reverse is compatible, however, with the 1st Law. So there must be some other principle (like the 2nd Law) that governs the direction of processes.

   d) Also note in the above example that some ability to do work has been lost. For instance we could have put a piston in the volume and allowed the expansion of the gas to do work to raise a weight.
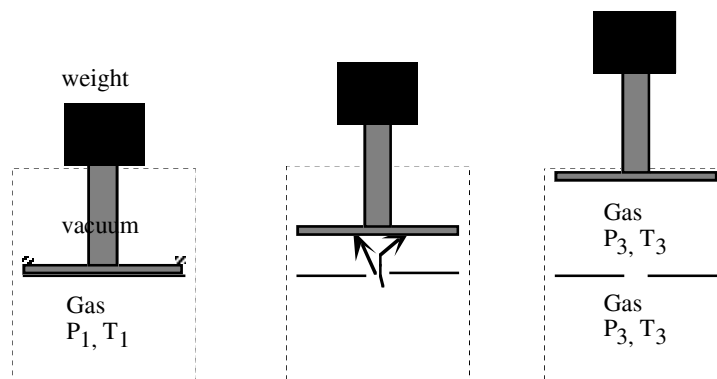
   e) If we carefully extract the maximum possible work from the system with a piston, then it is conceivable to think that we could reverse the process and

put that work back into the system and everything (the system and the surroundings) would be back to the initial state.

f)   But if we let the gas undergo a free expansion, we lose some ability to get work out of the system. The property that is used to measure the 'change in ability to get work out of a system' is the entropy.

g)   For reversible processes (the most efficient processes possible), the net change in entropy in the universe (system + surroundings) is zero.

h)   Phenomena that introduce irreversibility and inefficiency are: friction, heat transfer across finite temperature differences, free expansion, ...

IV. Brief glossary of new terms

- System

- State

- Equilibrium

- Pure substance

- Intensive

- Extensive

- Specific volume

- Thermally perfect gas

- Heat

- Adiabatic

- Isobaric

- Isothermal

- Internal energy

- Enthalpy

- Static

- Stagnation

- Entropy

- Reversible

- Irreversible

- Isentropic

- Specific heat

- Cycle