Lecture Ch. 2a

- Energy and its properties
  - State functions or exact differentials
  - Internal energy vs. enthalpy
- First law of thermodynamics
- Heat/work cycles
  - Energy vs. heat/work?
  - Adiabatic processes
  - Reversible "P-V" work
- Homework problem Ch. 2, Prob. 2

Curry and Webster, Ch. 2 pp. 35-47
Van Ness, Ch. 2

Internal Energy vs. Enthalpy

It is convenient to define a new function called the *enthalpy*, H, by

$$H = U + pV \qquad (2.12)$$

- Difference b/w U and H
  - U depends on v $du = \left(\frac{\partial u}{\partial T}\right) dT + \left(\frac{\partial u}{\partial v}\right) dv$
  - H depends on p $dh = \left(\frac{\partial h}{\partial T}\right) dT + \left(\frac{\partial h}{\partial p}\right) dp$
- Specific heats [a.k.a. heat capacity]
  - c_v is constant v $c_v = \frac{dq_v}{dT} = \frac{\partial u}{\partial T}$ (2.15a)
  - c_p is constant p $c_p = \frac{dq_p}{dT} = \frac{\partial h}{\partial T}$ (2.15b)

Heat Capacity

$$du = c_v\,dT \qquad (2.16)$$
$$dh = c_p\,dT$$

How does c_v differ from c_p quantitatively? In a constant-pressure process, some of the added heat must be expended in doing work on the surroundings, while in a constant-volume process, all of the heat is devoted to raising the temperature of the substance. Therefore it takes more heat per unit temperature rise at constant pressure than at constant volume, and $c_p > c_v$. The difference between c_p and c_v can be evaluated from

$$c_p - c_v = \left(\frac{\partial h}{\partial T}\right)_p - \left(\frac{\partial u}{\partial T}\right)_v$$

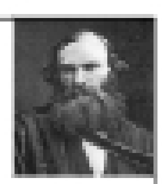
For an ideal gas

- Simplify to

1. The equation of state is $pv = RT$.
2. The internal energy is a function of its temperature alone [$du = c_v\,dT$; $dh = c_p\,dT$].
3. The specific heats are related by $c_p - c_v = R$.

- [Types of processes]
  - Constant pressure
  - Constant volume

Lord Kelvin (a.k.a William Thomson)



James P. Joule

- *The First Law of Thermodynamics*

$$dU = dQ + dW \qquad (2.7)$$

- *Consequences*

Uniqueness of work values	$W_{rev} = -\int p\,dV$	Reversible
Definition of energy	$Q = 0 \Rightarrow \Delta E = W$	Adiabatic
Conservation of energy	$Q = 0, W = 0 \Rightarrow \Delta E = 0 \Rightarrow E_f = E_i$	State function
Impossibility of perpetual motion machine	$Q = 0, \Delta E = 0 \Rightarrow W = 0$	See also 2nd law!
(Relativity)	$\Delta E = mc^2$	Proof follows...

Other Kinds of Energy

- In addition to changes in internal energy, a system may change
  - Potential energy for height change Δz
  - Kinetic energy for velocity change Δv
  - Nuclear energy for mass change Δm

$$\Delta E = \Delta U(p,V,T) + mg\Delta z + \frac{1}{2} m\Delta v^2 - c^2\Delta m = Q + W$$

if $\Delta E = \Delta U(p,V,T)$, then $\Delta U(p,V,T) = Q + W$

Van Ness, p. 13

Work

- Expansion work W=-pdV or w=-pdv
  - Lifting/rising
  - Mixing
  - Convergence
- Other kinds of work?
  - Electrochemical (e.g. batteries)

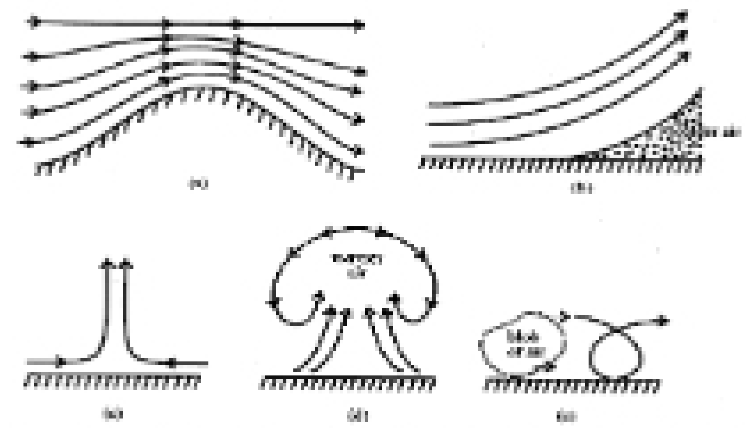


Figure 2.1 Rising motion occurs in the atmosphere due to (a) orographic lifting, (b) frontal lifting, (c) low-level convergence, (d) buoyant rising of warm air, and (e) mechanical mixing. Expansion work is done by an air parcel when it rises.

Cycles

- Work and heat are path-dependent transfers
  - W work
  - Q heat

$$\oint dw \neq 0 \qquad \oint dQ \neq 0$$

- State functions are unique "states"
  - U internal energy
  - H enthalpy
  - η (also S) entropy
  - A Helmholtz free energy

$$du = dq + dw$$

$$0 = \Delta U_{cycle}(A \rightarrow B \rightarrow A) = \oint dU$$

Exact Differentials

- State functions are exact differentials

An exact differential $d\xi$ has the following properties:

1. The integral of $d\xi$ about a closed path is equal to zero ($\oint d\xi = 0$).
2. For $\xi(x,y)$, we have $d\xi = [\partial\xi/\partial x]\,dx + [\partial\xi/\partial y]\,dy$ where x and y are independent variables of the system and the subscripts x and y on the partial derivatives indicate which variable is held constant in the differentiation.

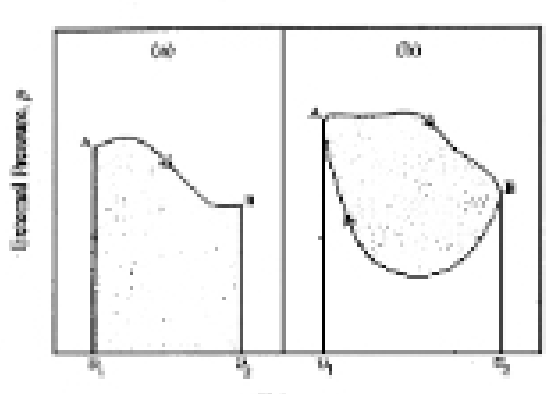


Figure 2.2 (a) The amount of work done in the expansion from v_1 to v_2 is equal to the area under the curve. In (b), the system is compressed back to v_1 via a different process. Even though the system has returned to its initial state, net work has been done, as indicated by the shaded area between the two curves.

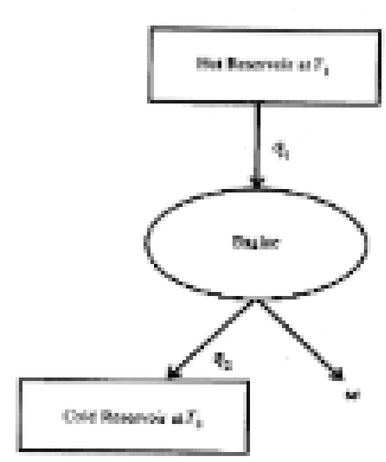
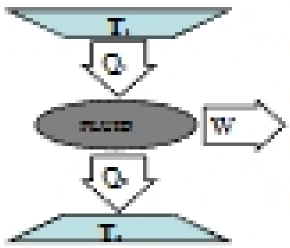


Figure 2.6 Carnot heat engine. Heat q_1 is brought from the hot reservoir to the engine. The engine does work w and rejects heat q_2 into the cold reservoir.

Heat/Work Cycles

Carnot was an engineer in Napoleon's defeated army with an interest in engines.

- The efficiency with which work is accomplished in a reversible cyclic process depends only on the temperature of the reservoirs to which heat is transferred



THE CARNOT CYCLE

STEP 1: Expand isothermally and reversibly at T_1

STEP 2: Expand adiabatically and reversibly

STEP 3: Compress isothermally and reversibly at T_2

STEP 4: Compress adiabatically and reversibly

Efficiency:

$$\eta = 1 - \frac{T_{Cold}}{T_{Hot}}$$

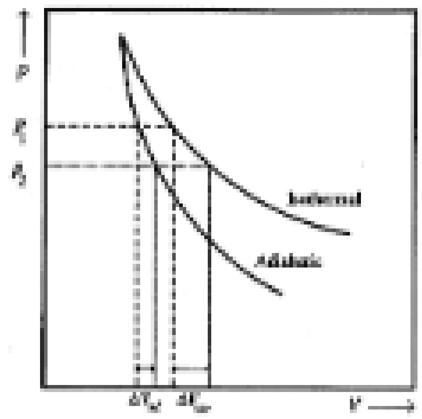
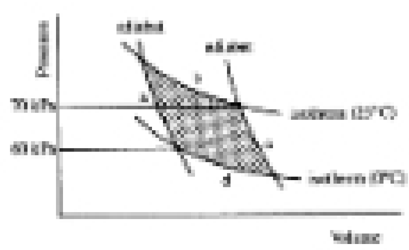


Figure 2.3 Isothermal expansion compared with a reversible adiabatic expansion. For a given drop in pressure, $\Delta V_{iso} > \Delta V_{adi}$, since during the adiabatic expansion, the temperature also decreases.

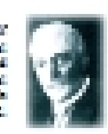
P-V diagrams of work

- Work is determined by pathway



Other Work Cycles

Nikolaus Otto developed the Otto cycle in 1876.



Rudolf Diesel developed the Diesel cycle in 1892.

The Otto Cycle works by compressing a mixture of air and fuel in a piston and then igniting the mixture with a spark.

The Diesel Cycle works by compressing air and then adding fuel directly to the piston. The compressed air then combusts the mixture.

The compression ratio of the Diesel Cycle ranges from 14:1 to 25:1, while the Otto Cycle range is significantly lower, from 8:1 to 12:1. The defining feature of the Diesel engine is the use of compression ignition to burn the fuel, which is injected into the combustion chamber during the final stage of compression. This is in contrast to a gasoline engine, which utilizes the Otto cycle, in which ignition is initiated by a spark plug following the injection and compression of a fuel/air mixture.

Efficiency:

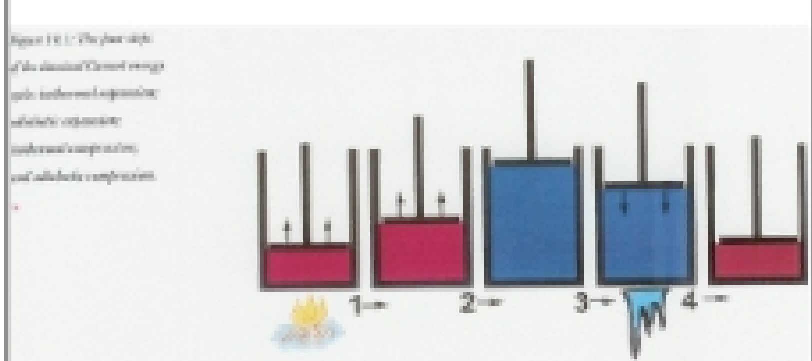
$$\eta = 1 - \frac{T_d - T_a}{T_c - T_b}$$

Efficiency:

$$\eta = 1 - \frac{1}{\gamma}\left(\frac{T_B - T_C}{T_A - T_D}\right)$$

$\gamma = \frac{5}{3}$ for monoatomic ideal gas

4 Steps of Carnot "Engine"



1:Add Heat (isothermally) 2:Adiabatic 3:Lose Heat (isothermally) 4:Adiabatic

Hurricane as Carnot Cycle