Homework Schedule
Email Single PDF to ajlee@ucsd.edu

- Due Oct. 8 (Monday, 12 noon)
  - Ch. 1, Problem 11
  - Ch. 2, Problem 2
- Due Oct. 22 (Monday, 12 noon)
  - Ch. 3, Problem 1, 2 (typo in answer key), 3
  - Ch. 4, Problem 4, 5
- Midterm Oct. 31 (in class)
- Due Nov. 5 (Monday, 12 noon)
  - Ch. 5, Problem 3, 7 (erratum in 7d)
- Due Nov. 14 (Wednesday, 12 noon)
  - Ch. 6, Problem 4, 6
- Due Nov. 19 (Monday, 12 noon)
  - Ch. 7, Problem 3 (not graded, outline approach only, discuss)

What did we learn in Ch. 1?

- What P, T, U are for a fluid
- What an ideal gas is
- How P, T, v relate for an ideal gas (and we call this relationship an equation of state)
- What chemical components constitute the atmosphere (for homosphere <110 km)
- What the hydrostatic balance is
- How p, T vary with z for observed, "standard," isopycnic, isothermal, constant lapse-rate atmospheres

Lecture Ch. 2a

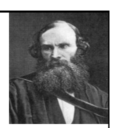
- Energy and heat capacity
  - State functions or exact differentials
  - Internal energy vs. enthalpy
- 1st Law of thermodynamics
  - Relate heat, work, energy
- Heat/work cycles (and path integrals)
  - Energy vs. heat/work?
  - Adiabatic processes
  - Reversible "P-V" work → define entropy

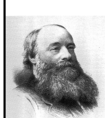
Curry and Webster, Ch. 2 pp. 35-47
Van Ness, Ch. 2

Key Combined 1st+2nd Law Results

- 1st Law: du=dq+dw; u is exact — Eq. 2.8
  - $du=dq_{rev}-pdv$ (expansion only) — p. 56
- Define Enthalpy: H=U+PV — Eq. 2.12
  - dh=du+pdv+vdp
- 2nd Law: $[dq_{rev}/T]_{int.cycle}=0$ — Eq. 2.27
- Define Entropy: $d\eta=dq_{rev}/T$ — Eq. 2.25a
  - $Td\eta=dq_{rev}$
  - $du=Td\eta-pdv$
- Define Gibbs: $G=H-T\eta$ — Eq. 2.33
  - $dg=dh-Td\eta-\eta dT=(du+pdv+vdp)-Td\eta-\eta dT$
  - $dg=du-(Td\eta-pdv)+vdp-\eta dT=vdp-\eta dT$ — p. 58
- $(\delta p/\delta t)_g=\eta/v$ — Eq. 2.40

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	$W_{rev} = -\int pdv$	Reversible
Definition of energy	$Q=0 \Rightarrow \Delta E = W$	Adiabatic
Conservation of energy	$Q=0, W=0 \Rightarrow \Delta E = 0 \Rightarrow E_2 = E_1$	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 for hmwk…

Other Kinds of Energy
What is the difference between E and U?

- 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

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

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

Van Ness, p. 13

Exact Differentials

- State functions are exact differentials

tween them. The first law thus states that although dQ and dW are not exact differentials, their sum $dU = dQ + dW$ is an exact differential and thus a thermodynamic state variable.

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.

Heat Capacity

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 $du = \left(\frac{\partial u}{\partial T}\right) dT + \left(\frac{\partial u}{\partial v}\right) dv$ From 1[st] Law (i.e. U is exact differential
  - H depends on p $dh = \left(\frac{\partial h}{\partial T}\right) dT + \left(\frac{\partial h}{\partial p}\right) dp$ Defined above
- 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

For all gases:

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

$$dh = c_p\,dT + \left(\frac{\partial h}{\partial p}\right)_T dp$$

For an ideal gas, it has been shown experimentally that $(\partial u/\partial v)_T = 0$, so that internal energy is a function only of temperature for an ideal gas, i.e., $u = u(T)$. It can also be shown that $(\partial h/\partial p)_T = 0$ and $h = h(T)$. This implies that for ideal gases

For ideal gases:

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

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

Work

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

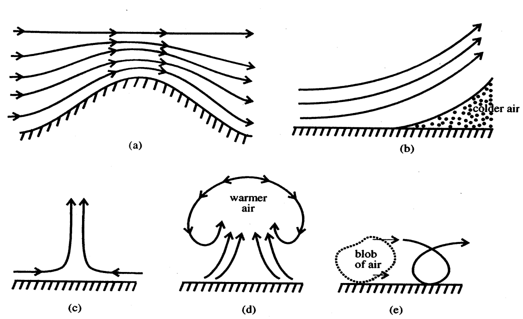


Figure 2.1 Rising motion occurs in the atmosphere due to (a) orographic lifting, (b) frontal lifting, (c) low-level convergence, (d) buoyant rising of warm air, and (e) mechanical mixing. Expansion work is done by an air parcel when it rises.

Cycles

- Work and heat are path-dependent transfers
  - W work $\oint dw \neq 0$
  - Q heat $\oint dQ \neq 0$
- State functions are unique "states"
  - U internal energy $du = dq + dw$
  - H enthalpy $0 = \Delta U_{syst}(A \to B \to A) = \oint dU$
  - η (also S) entropy
  - A Helmholtz free energy
  - G Gibbs energy

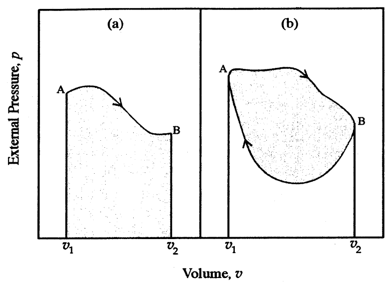


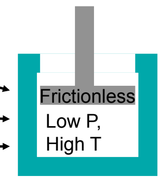
Figure 2.2 (a) The amount of work done in the expansion from v_1 to v_2 is equal to the area under the curve. In (b), the system is compressed back to v_1 via a different process. Even though the system has returned to its initial state, net work has been done, as indicated by the shaded area between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

Reversible-Adiabatic-Work

Reversible
mass is conserved

Ideal Gas

Adiabatic
thick walls



$W = -pdv$

$\frac{p_1 v_1}{T_1} = R = \frac{p_2 v_2}{T_2}$

$Q = 0$

First Law $\Delta u = Q + W$

Internal Energy $\Delta u = c_v dT$

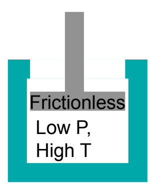
Reversible, Adiabatic $\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/c_p}$

Reversible-Adiabatic-Work

Reversible
mass is conserved

Ideal Gas

Adiabatic
thick walls



$W = -pdv$

$\frac{p_1 v_1}{T_1} = R = \frac{p_2 v_2}{T_2}$

$Q = 0$

$-pdv = c_v dT$

$-\left(\frac{RT}{v}\right)dv = c_v dT$

$-\int_1^2 R\frac{dv}{v} = \int_1^2 c_v \frac{dT}{T}$

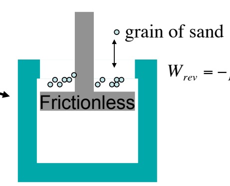
First Law $\Delta u = Q + W$

Internal Energy $\Delta u = c_v dT$

Reversible, Adiabatic $\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\boxed{R/c_p}}$

Reversible Processes

Reversible
mass is conserved



$W_{rev} = -pdv$

- Always at or infinitesimally close to equilibrium
- Infinitesimally small steps
- Infinite number of steps
- Each step can be reversed with infinitesimal force

Lecture Ch. 2b

- Entropy
- Second law of thermodynamics
- Maxwell's equations
- Heat capacity
- "Meteorologist's entropy"

Curry and Webster, Ch. 2 pp. 47-62
Van Ness, Ch. 5-7

Entropy

- Is there a way to quantify "useful" energy?
- Need a measure that is conserved, exact, unique
- While Q is not exact, Q_{rev} is exact
  - Reversible heat is limit of maximum work done
  - Since path is specified, cyclic integral is 0

There exists an additive function of state known as the equilibrium entropy, which can never decrease in a thermally isolated system.

Curry and Webster, Ch. 2 pp. 47-62
Van Ness, Ch. 5-7

Entropy

1st Law

Consider the first law of thermodynamics in enthalpy form (2.18b) for a reversible process:

$$dq = c_p\,dT - v\,dp$$

Reversible heating is an abstract concept, whereby heating of a system occurs infinitesimally slowly through contact with an infinite heat reservoir. For the reversible expansion of an ideal gas, we may substitute for the specific volume from the equation of state and divide by temperature

$$\frac{dq}{T} = c_p\frac{dT}{T} - R\frac{dp}{p} = c_p\,d(\ln T) - R\,d(\ln p) \qquad (2.23)$$

The two terms on the right-hand side of (2.23) are by definition exact differentials, and their sum must also be an exact differential. Therefore dq/T is an exact differential, i.e.,

$$\oint\left(\frac{dq}{T}\right)_{rev} = 0 \qquad (2.24)$$

where the subscript *rev* emphasizes that this relationship holds only for a reversible process. Dividing heat by temperature converts the inexact differential dq into an exact differential. We can now define a new thermodynamic state function, the *entropy*, η, with units J K^{-1} kg^{-1}, to be

Definition

$$d\eta = \left(\frac{dq}{T}\right)_{rev} \qquad (2.25a)$$

Second law of Thermodynamics

- Heat cannot pass of itself from a colder body to a hotter body.

19°C	21°C	$\xrightarrow{\text{not possible}}$	10°C	30°C

- A system left to itself cannot move from a less ordered state to a more ordered state.

room containing air	$\xrightarrow{\text{not possible}}$	O_2 here	N_2 here

- The entropy of an isolated system cannot decrease.

$$\Delta S_{system} \geq 0$$

$$\Delta S_{system} = \int_{state\,1}^{state\,2}\frac{dQ_{rev}}{T_{system}}$$

Clausius' Inequality

$$\boxed{\Delta\eta_{tot} \geq 0}$$

which is known as *Clausius' inequality*. For a reversible process we cannot have $\Delta\eta_{tot} > 0$, since we would have $\Delta\eta_{tot} < 0$ upon reversing the process, which would violate Clausius' inequality. Therefore, $\Delta\eta_{tot} = 0$ for all reversible changes. For the

No process exists in which heat is extracted from a source at a single temperature and converted entirely into useful work, leaving the rest of the world unchanged.

Consider the basic thermodynamic relations (2.31), (2.32), (2.34), and (2.36):

$$\begin{aligned} du &= T\,d\eta - p\,dv \\ dh &= T\,d\eta + v\,dp \\ da &= -\eta\,dT - p\,dv \\ dg &= -\eta\,dT + v\,dp \end{aligned}$$

If we set the left-hand sides of these equations equal to zero, we obtain

$$\left(\frac{\partial\eta}{\partial v}\right)_u = \frac{p}{T} \qquad (2.37)$$

$$\left(\frac{\partial\eta}{\partial p}\right)_h = -\frac{v}{T} \qquad (2.38)$$

$$\left(\frac{\partial v}{\partial T}\right)_a = -\frac{\eta}{p} \qquad (2.39)$$

At dg=0,
we get ndT=vdp
or (dp/dT)$_g$ =n/v

$$\left(\frac{\partial p}{\partial T}\right)_g \cancel{=-}\frac{\eta}{v} \qquad (2.40)$$

typo in book

Maxwell's Equations

Since du, dh, da, and dg are exact differentials, they obey the Euler condition (2.9). Therefore from (2.31), (2.32), (2.34) and (2.36) we obtain the following set of useful relations called *Maxwell's equations*:

$$\left(\frac{\partial T}{\partial v}\right)_\eta = -\left(\frac{\partial p}{\partial \eta}\right)_v \qquad (2.49)$$

$$\left(\frac{\partial T}{\partial p}\right)_\eta = \left(\frac{\partial v}{\partial \eta}\right)_p \qquad (2.50)$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial \eta}{\partial v}\right)_T \qquad (2.51)$$

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial \eta}{\partial p}\right)_T \qquad (2.52)$$